Commentary

PAYING YOUR MONEY

There are various ways of paying your money, some more lethal than others. Economists devote treatises to taxation, advertising agents devise ingenious schemes to emphasize the ' insatiability of human wants ', merchants cultivate and develop the public taste. Goods and services come in various and divers forms and they are paid for in different and dismal ways. A newspaper or a pint of old and mild is usually paid for ' on the nail '—but not always—as a bus journey is paid or a cinema seat. Houses are frequently bought on credit and the extensive development of hire purchase is one of the social features of the age. 'It used to be called ' the never-never ' but is rising rapidly in the social scale and is now quite as virtuous as a bank overdraft. Many services are paid for out of rates and taxes, the police, education and, more recently, health; the armed forces probably formed the first nationalized industry. A levy is imposed and the proportion to be devoted to each is determined by ' the due process of parliament '. In some cases payment is made by a system of licenses, marriage licenses, dog licenses, radio licenses, television licenses. No attempt is made to estimate the value of the privilege to the individual and each must decide for himself whether it is worth it. There are frequent complaints; extracting money is usually a noisy business.

Television is big business. It is big business for the electronics industry. It is bigger business for the sellers of wares, domestic wares, consumable goods of all kinds and for industrial and political wares. It is the biggest mass medium of them all and it is growing fast. The history of Independent Television in this country emphasizes this, and the potential for the advertiser and the educator is stupendous. All other mass media predicate some measure of literacy and effort on the part of the target; television is delivered at your fireside and all you need is *either* eyes that see or ears that hear. At present television is paid for by license, at a cost which is largely nominal in view of what is provided and, in the case of the I.T.V. service, by payment for advertising time.

It is fascinating to consider the problem and the possibility that television should, like electricity and gas, be paid for on a ' consumer basis ', that is that the viewer pays according to his use. If the television service is furnished by a system of central, domestic-wired supplies then of course there is no technical problem. A slot-machine of a conventional type governs the hours of use. But this would be expensive and, more important, avoids the primary problem of abandoning the greatest merit of television, namely the flexibility conferred by being broadcast. Reception needs no central, domestic-wired supply. Even in this case the question arises as to whether a higher (or lower) rate should be charged for programmes at the popular hours of viewing.

The kernel of the problem is at the receiver, if you haven't paid your money, you get no choice; the programme is incomprehensible. Certainly to code or ' scramble ' the transmitted programme and fit a decoder to the receiver, gated by money, presents a difficult but by no means intractable problem to a communications engineer. The key is surely in the time-base at the receiver and the synchronizing or marker pips. If the signal is not synchronized, the vision is ruined. Moreover the density of marker pips can be varied from time to time so that the cost rate per unit time of viewing can be altered. In principle there is bound to be a slight decrease in the signal-to-noise ratio because of the increased ' information ' required for each picture but this will be small. Collecting the money is not likely to present a serious problem and ' season tickets ' are easy to supply.

If television *is* to be paid on the nail, this will have an effect on its impact. It is always the man behind the counter who gets the full benefit of wrath when the goods are shoddy. If the public pays as it goes, it will be more discriminating and switch off more frequently. The recent magistrate's case of the zombie-boy who watched all day and every day is unlikely to arise. If father doesn't know where the fuse is, mother will certainly run out of shillings. But advertisers are the prey of the mass market and the danger is that programmes degenerate to the lowest common multiple of human pastime. And the lowest common multiple is the deadly enemy of the highest common factor.

Second Prize in the Waverley Gold Medal Essay Competition

THE IRRADIATION OF PLASTICS

T. R. MANLEY

A. Reyrolle and Co. Ltd, Hebburn, Co. Durham

WHEN any substance is irradiated it absorbs energy from the incident neutrons or rays. This energy produces chemical changes, the most important of which, with regard to plastics, are cross linking and polymerization. Polymerization is the formation of very large molecules (polymers) by the linking together of a number of identical small molecules (monomers) and if two kinds of monomer are involved the process is known as copolymerization. When a copolymer has a simple material, such as water, as a by-product it is known as a condensation polymer.

Thermoplastic materials soften on heating because the polymers of which they are composed can easily move relatively to each other. If these polymers are joined by chemical bonds this movement is hindered, so that the material is no longer thermoplastic or at least the softening temperature is raised, and the material is said to be cross linked.

At one time it was thought that polymers could be divided into two classes depending on whether they cross linked or were degraded by radiation. Degradation occurs when the polymer breaks up into smaller molecules; in passing it may be noted that under radiation the bonds broken are within the monomer units and not at the links between the units as in thermal degradation.

E. J. LAWTON irradiated a number of polymers with high energy electrons and allocated them to each class as follows:

Cross linked	*Degraded*
Polystyrene	Perspex
Nylon	P.V.C.
Natural Rubber	Butyl rubber
G.R.S. rubber	Cellulose
Hypalon	PTFE or " Fluon "
Neoprene	
Polyesters	
Polythene	
Methyl silicones	

Unfortunately these divisions were blurred by K. LITTLE who found that nylon and the polyester, terylene, were degraded in the British experimental (zero energy) pile B.E.P.O. at Harwell. It is now known that in any polymer radiation has several other effects in addition to cross linking but cross linking is the most important effect in the case of the polymers listed in the first column.

Polymerization

Most modern plastics are made by free radicals. A free radical is a fragment of a molecule which readily adds on to other molecules transferring to them its activity, somewhat in the manner of a magnet and iron filings. Thus free radicals rapidly convert monomers into chains of polymers. Radiation can produce free radicals both in monomers and polymers and may therefore be used for polymerization, or to copolymerize other monomers on to a previously formed polymer. These copolymers are divided into two types, block and graft; the former is produced when the free radical arises from fracture of the main chain of the polymer, and the latter from fracture of the side chain. The term graft copolymer is however widely used for both types.

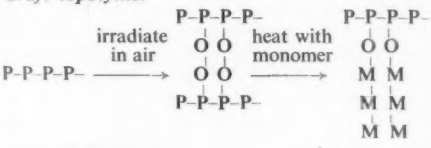
The simplest method of copolymerization is to dip the polymer into a monomer which penetrates the polymer and then to irradiate the whole. It is obvious of course that there will be a considerable amount of normal polymerization (homopolymerization) as well as copolymerization. An alternative procedure depends on the fact that the free radicals may exist for long periods in the polymer; one may irradiate a polymer and then immerse it in a monomer which is thereby grafted on to the polymer without any appreciable homopolymerization. This method, however, requires higher dosages than the first one.

The fact that irradiated molecules may react with atmospheric oxygen was utilized by A. CHAPIRO and his collaborators who irradiated polymers in air to form peroxides and then heated these peroxides in the presence of monomers, to give copolymers. (Thus he obtained the benefits of a peroxide catalyst without the disadvantages of having to add the catalyst residue.) This reaction is

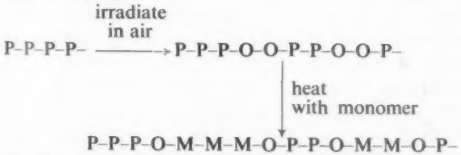
Sir Charles Darwin presenting the second prize to Mr T. R. Manley at the Royal Society of Arts on December 15th. Mr Manley is Chief Research Chemist at A. Reyrolle and Co. Ltd who are engaged in the production of electrical switchgear, generators, domestic equipment, etc.

illustrated in the following scheme where the polymer molecules are represented by P and the monomers by M.

Graft copolymer



Block Copolymers



By this method copolymers containing only five per cent of the original polymer have been prepared. The properties of copolymers in most cases are intermediate between those of each polymer.

The chief attractions of graft copolymerization by radiation are that the dose rates are about one tenth of those required for cross linking or vulcanization and that it is possible for the first time to copolymerize condensation polymers and free radical initiated polymers.

The largest consumers of radiation where cross linking is the desired main effect, are likely to be polythene, natural rubber and silicones.

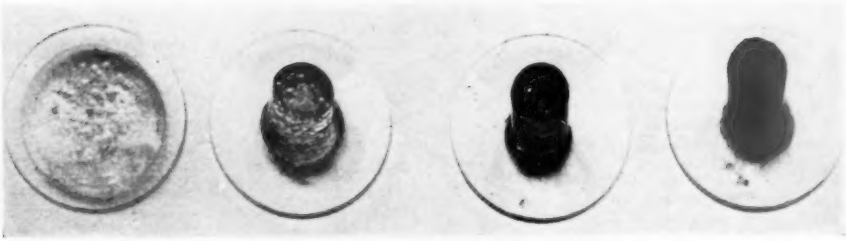
Radiation Stability

In choosing plastics for radiation processing those requiring low dosages are obviously preferable. On the other hand it is sometimes desirable, for example in constructional materials for nuclear reactors, to have plastics stable to radiation. Plastics whose molecules include phenyl groups have increased radiation stability. This effect was established by A. CHARLESBY who found that the energy required per cross link in polythene, to be about one per cent that for polystyrene which has a similar structure apart from containing a phenyl group (see for example *Figure 1*). Silicones containing phenyl groups are unaffected by radiation doses which cause others to cross link and gel. Plastics with low radiation stability include halogenated compounds, butyl rubber and Perspex.

Inorganic fillers such as asbestos produce a more radiation resistant material but pigments, such as titania, reduce the radiation resistance.

Polythene

Polythene was the first commercial plastic to have its properties improved by radiation. The dielectric properties of polythene are outstanding but it has the disadvantage of being soluble in transformer oil, the most commonly used liquid insulant. In 1952, A. Charlesby irradiated polythene in the B.E.P.O. pile and obtained a material with a higher softening point due to the cross linking of the long chain molecules (see *Figure 2*). By courtesy of Dr Charlesby and the United Kingdom Atomic Energy Authority samples of irradiated polythene were obtained. The first was an opaque, yellowish and somewhat rubbery rod which had received 200 megarads. (One megarad represents an energy absorption of 10^8 ergs per gram of material.) After seven days immersion in oil at 60°C it had increased in weight but retained its physical characteristics whereas a sample which had not been irradiated had completely dissolved.



(a) (b) (c) (d)

Figure 1. Effect of heating polystyrene for 30 minutes at 250°C—(a) radiation dose nil, no cross links per molecule; (b) radiation dose 0·6 megarads and 0·6 cross links per molecule; (c) radiation dose 2 megarads and 2 cross links per molecule; and (d) radiation dose 6 megarads and 6 cross links per molecule (by courtesy of the U.K.A.E.A.)

Further samples were obtained, one of which had received 750 megarads and was substantially unchanged after 15 days in oil at 110°C. The bursting strength of polythene film 0·005 in. thick which was exposed to 200 megarads was increased by 20 per cent; after 48 hours in oil at 60°C the bursting strength was the same as that of unirradiated film. Since polythene is oxidized by radiation in air some deterioration in dielectric properties is to be expected. In the present instance however the difference in dielectric constant between the irradiated and control samples was insignificant.

In addition to improving the oil resistance, the irradiation of polythene greatly increases its softening point; values of up to 200°C were obtained. This greatly widens its useful range for capacitors and small transformers, and makes it very useful for wire insulation as it is not melted by short term contact with molten solder. In cable manufacture advantage is taken of the fact that prestressed irradiated polythene film will shrink on heating to 150°C and adhere to itself under pressure to give a moisture proof covering. This property is also of use for other wrapping applications. Outside the electrical industry the fact that the material can be sterilized opens up markets in biological equipment and the food industry.

Silicones

As silicone rubbers can be produced by dosages of the order of one megarad and in view of the great improvement in properties, radiation cured products are expected to have a wide market. The silicones are promising as materials for irradiation because in many cases their best properties are not realized unless they can be cured at elevated temperatures usually 250°C. This rules out the possibility of applying them to materials such as bakelized paper which are widely used in the electrical industry. Radiation curing would enable a silicone to be applied to such material giving a much improved product for little increase in cost. It would of course be necessary to avoid silicone fluids containing phenyl unless a high degree of radiation were permissible.

Rubber

As problems of ageing and wear have long been associated with sulphur vulcanized tyres there are obvious advantages which would be expected in a radiation vulcanized tyre. This was recognized as long ago as 1933 when a patent was issued for the vulcanizing of rubber by means of high energy electrons. Work is proceeding in this country and in America whence C. H. STOCKMAN reports that tyres vulcanized by spent fuel elements have been shown in laboratory tests to have better ageing properties and to be more abrasion resistant than the normally vulcanized tyres. A dose of 50 megarads was employed, which makes it uneconomic to produce tyres by this method at present, but with cheaper sources, the more efficient use of radiation, or by copolymerization a large market for isotopes seems to be assured.

Polymers Formed by Radiation

Any plastic polymerized by free radicals may be made by radiation. These include the thermoplastics such as polythene, polypropylene, Perspex, polystyrene; copolymers such as polyester resins for electrical insulation, and synthetic rubbers.

Typical yields of plastics are ten per cent per megarad for polystyrene and 84 per cent per megarad for Perspex. These yields were obtained at 70°C; they would be reduced by a factor of twenty if the temperature were reduced by 100°C. For polythene, the energy required is about ten megarads; this varies with the purity of the ethylene and with the presence of oxygen. The use of radiation enables much closer control to be exercised on the degree

of polymerization, and in addition radiation cured polymers are free from traces of residual catalyst which adversely affect the final properties. In the low pressure synthesis of polythene for example the removal of the catalyst from the finished product is a major difficulty which suggests that this type of polythene may be restricted to non-electrical applications.

Residual catalyst is also a cause of thermal instability in polymers and the improvements in the heat distortion temperatures obtained by radiation curing may be seen in *Table 1*. By using radiation certain polymerizations may be performed which are impossible by other methods. These include

(*i*) Polymerization of solid materials, for example, acrylamide;

(*ii*) Polymerization of fluorocarbons such as perfluoropropylene;

(*iii*) Copolymerization of polymers like P.T.F.E. with polystyrene;

(*iv*) Copolymerization of condensation with free radical polymers, such as nylon with polythene.

Further Applications of Radiation

Further applications of radiation will now be considered.

Low Temperature Polymerization

Since the irradiation may produce free radicals even at very low temperatures this gives an opportunity to polymerize materials at much lower temperatures than was hitherto possible. Advantage has been taken of this fact to apply a protective coating to germanium diodes which are very sensitive to heat. The germanium element is dipped in a styrene–alkyd liquid and the copolymer is formed by the action of high energy electrons giving a moisture proof barrier for the diode. It is stated that the properties of the germanium are not impaired by the irradiation. This would not hold if the irradiation were to come from either a gamma source or pile radiation, as gamma rays convert *n*-type germanium to *p*-type.

Table 1. Heat distortion temperature (°C)

Cure \ Polymer	Perspex	Polystyrene	Polymethylstyrene
Radiation	150	105	187
Normal	130	85	147

Graft Copolymerization

P.T.F.E. is widely used for its chemical inertness but it has a corresponding disadvantage in that no satisfactory adhesive for it is known. By grafting to P.T.F.E. polystyrene or another readily adherent material the usefulness of P.T.F.E. is greatly increased. Conversely it is possible to put an inert film of P.T.F.E. on to polythene and other plastics which are rapidly attacked by solvents or corrosives. If it is desired to modify the properties of any polymer this may be done by suitable choice of another monomer for block copolymerization. There would appear to be no limitations, apart from cost, to the specifications which could be met by this method.

Figure 2. Effect of irradiating polyethylene—the irradiated bottle (RIGHT) *was immersed in oil at 150°C for six minutes and the unirradiated bottle* (LEFT) *collapsed in 10 sec under these conditions (by courtesy of Metropolitan-Vickers)*

Degraded Polymers

Although polymers which are degraded by radiation will be useful as sources of molecules of definite size for research and medicinal purposes, such as production of blood plasma substitutes, they might not appear to have any value as plastics. This view is however too pessimistic. A. Charlesby states that P.T.F.E. after receiving dosages of the order of one megarad may be moulded at 200°C or less, well below its normal moulding temperature. He also improved the solvent resistance of various plastics by means of a radiation dosage too low to affect their mechanical properties. The same author has suggested that foamed Perspex produced by heating irradiated specimens may be used as an insulating medium but it is unlikely to be able to compete with other foams.

Safety

Since the sources used will deliver at least 10,000 rads whilst the lethal dose for a man is only 500 rads, remote handling through shielding must be used. On account of the publicity which has been afforded to radioactive poisoning from the ' fall out ' of atomic weapons it would be wise to ensure not only that high safety standards are being maintained but that workers in contact with radioactivity are

aware that they are so maintained. The standards of the U.K.A.E.A. which have enabled the authority to preserve an accident rate well below the industrial average, should be enforced where applicable.

Costs

Much of the work up to date has been performed in atomic piles such as B.E.P.O. which were designed for research and are quite uneconomical for large scale irradiation. Reactors have been designed which will produce radiation at competitive prices. At present the high capital requirements have caused industrialists to wait for more information on potential markets. An American reactor, for production of cobalt 60 radiation sources, is scheduled to start in 1958 an annual production of one million curies at two dollars per curie.

Particle accelerators are now economic for special applications such as the cross linking of polythene. For development work a 4 million electron volt machine may be hired for £50 per day. This will, for example, cure 80 lb of rubber per hour at a cost of 1*s* 8*d* per lb. Rubber requires 5 megarads for curing; other dosages may be given for other materials with proportionate variations in output and costs. For irradiation of moulded articles the efficiency drops approximately 60 per cent.

Whilst accelerators may be more attractive than isotope sources at present it is considered that the increasing availability of the latter will reverse this, especially for bulk processing.

It is difficult to obtain true costs for isotopes and spent fuel elements produced in the reactors at present under construction but it is to be expected that the Atomic Energy Authority will keep prices low in order to avoid disposal problems. The United States Atomic Energy Commission recently reduced the prices of some of its isotopes by over 95 per cent and a member of the Commission forecast the prices in *Table 2* will be reached ' in the next decade '. At these prices a point source of cobalt 60 providing one megarad per hour one inch from the source would cost £10. This represents a ' rock bottom price ' and it should be noted that the intensity drops rapidly with the distance from the source.

Several suitable arrangements for isotope sources have been described including one to give a dose of one megarad at a cost of one penny per pound. In addition to the price of the source the efficiency has an obvious influence on costs. The speed at which the dose is given and the operating temperature have marked effects on the rates of polymerization, degradation and cross linking.

Table 2. Predicted prices for isotopes in dollars per curie

Cobalt 60	0·06
Caesium 137	0·3
Iodine 131	0·0004
Sulphur 35	0·005

A further factor is the arrangement of the source. M. MAGAT stated that seven 15 curie sources could be arranged to produce 25 tons per annum of perspex at 60°C but this output is only doubled if the source is quadrupled.

Several investigators have obtained yields of polythene, by radiation of ethylene, that were high enough to consider the process to be economically feasible. There would appear however to be better prospects for radiation produced polymers from higher olefins such as propylene. Whilst it is true that there is a very large market for polythene there are several processes available for this material. Polypropylene on the other hand is a new material and is likely to be more expensive. It should be more suited as a product for a new technique and when further experience has been obtained greater availability of radiation should enable the ' atomic ' polymer to be produced on a large scale. In addition one can expect that the efficiency will rise with the increase in the molecular weight of the monomer. On the other hand polypropylene degrades more readily than polythene.

Conclusions

It can be concluded that

(*i*) Most conventional plastics may be made by irradiation usually with improved properties.

(*ii*) By the use of radiation plastics may be modified, again giving improved properties.

(*iii*) It is possible to produce by radiation entirely new plastics and new combinations of plastics with unique properties which cannot be produced by present methods.

(*iv*) The use of radiation is economic at present for only a few of these applications but the price of radiation is expected to fall sharply.

It is recommended that isotope sources be used for research and the development of further applications of radiation.

LARGE SCALE PREPARATION OF ULTRA-PURE GERMANIUM

J. M. WILSON

Standard Telecommunications Laboratories Ltd., Enfield, Middlesex

Germanium is required in an extremely pure state for use as a semiconductor. Its behaviour finally depends upon the presence of controlled amounts of certain impurities, such as the elements of Groups III and V, which respectively accept or donate electrons giving rise to *p*- and *n*-type material. Since the significant amounts of these impurities are of the order of one in 10^8 or 10^9 parts the requirements of semiconductor purity are stringent. Many special techniques and methods have been developed. This is the fifth article in the series on the technology of transistories; the sixth, on the preparation of ultra-pure silicon, will be published in the near future.

PRIOR TO 1947 germanium was regarded as a rare element and its properties and those of its compounds were only of academic interest. However, with the discovery of transistor action and the subsequent growth of a new industry, germanium has become an article of commerce with world production running at about 40,000 kg per annum.

Occurrence

There is almost as much germanium in the earth's crust as there is zinc and lead but there are few concentrated deposits and even in these germanium is only present as the secondary element. The most important minerals are complex sulphides. Argyrodite, a silver germanium sulphide, $4Ag_2S.GeS_2$, containing about six per cent germanium, occurs in Saxony and it was in this mineral that Winkler discovered and identified the new element in 1886. Two other minerals, germanite and renierite, are found in South-West Africa and the Belgian Congo. Germanite, which contains about ten per cent of the element, is essentially a copper iron thiogermanate, $7CuS.FeS.GeS_2$. Renierite, a complex sulphide of copper, iron, arsenic and germanium, contains about seven per cent of the latter.

Since these minerals are found only in association with others, the average germanium content of the deposits worked is considerably lower than that of the pure mineral. Many other ores contain trace amounts (0·01 to 0·1 per cent), but germanium is only obtained economically when some concentration occurs during the process for the recovery of the primary metal.

Some coals are also a source of germanium, the presence of germanium in some samples being demonstrated spectrographically by V. M. GOLDSCHMIDT[1] during his geochemical researches.

Production

The demands of the semiconductor industry for germanium have been satisfied by the recovery of the element as by-products of other industries. In the United States and France it is obtained during zinc processing, in England from certain flue dusts and in Belgium from concentrates from some African mines which are worked for their copper, zinc and lead ores.

Although the large scale production of germanium is of recent origin, the processes used are based on the characteristic chemical properties of the element, its dioxide, tetrachloride and disulphide, all of which have been known for a long time.

Chemical Properties of Germanium

Germanium has a silvery-white metallic appearance and is hard and brittle. Its density at 20°C is 5·35 and it melts at 958°C. At elevated temperatures it reacts with oxygen and chlorine to form the dioxide and tetrachloride respectively. In the ordinary chemical sense it is unaffected by air or moisture at room temperature and is unattacked by or dissolves only slowly in most acids and alkalis. The best solvents are aqua regia, three per cent hydrogen peroxide and mixtures of hydrofluoric acid and an oxidizing agent such as nitric acid or bromine.

Germanium tetrachloride may be prepared by burning germanium in chlorine gas or by distillation from a mixture of germanium dioxide and hydrochloric acid

$$Ge + 2Cl_2 = GeCl_4$$

$$GeO_2 + 4HCl \rightleftharpoons GeCl_4 + 2H_2O$$

Germanium tetrachloride is a colourless liquid (density 1·88; boiling point 83°C) which fumes in moist air due to the formation of the oxide and hydrochloric acid. The low boiling point, the solubility in

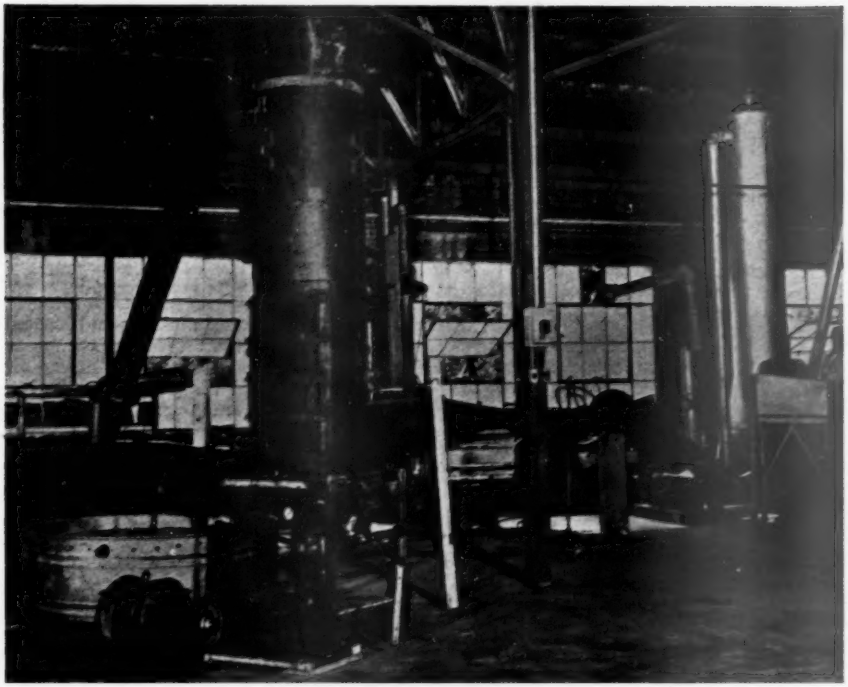


Figure 1. Pilot plant for smelting germaniferous ores—reproduced from J. Metals, N.Y. *4 (1952) 1132*

organic solvents such as benzene and carbon tetrachloride, and the ease of hydrolysis with water to the comparatively insoluble oxide, are typical properties of a covalent halide and they are utilized in the separation and purification processes.

Germanium dioxide is obtained by reaction of the metal with oxygen above 700°C, or by hydrolysis of the tetrachloride with water, as a white solid. The common metastable form (melting point 1115°C) has a quartz structure and is slightly soluble in water (0·4g in 100g at 20°C).

The oxide may be reduced with carbon under a layer of sodium chloride, but more usually hydrogen is used. The temperature of the hydrogen reduction must be controlled to prevent the volatilization of germanous oxide which is formed by reaction of germanium and germanium dioxide

$$GeO_2 + 2H_2 = Ge + 2H_2O$$
$$GeO_2 + Ge \rightleftharpoons 2GeO$$

Hydrogen sulphide precipitates germanium (IV) sulphide, GeS_2, as a white solid which is soluble in ammonium sulphide, from strongly acidic solutions containing germanium.

Extraction

Since the germanium content of the known sources is low the first step in the recovery processes is always concentration. This concentration sometimes occurs fortuitously as in gas works and zinc smelters. In other cases, such a step has to be introduced, as in the processing of the African ores. In all cases the germanium is ultimately separated by taking advantage of the volatility of the tetrachloride.

Germanite Ores

Before the second World War germanite was the main source of germanium and several recovery processes were published. Early methods which depended on obtaining germanium dioxide after decomposing the mineral with nitric and sulphuric acids suffered from the disadvantage of elaborate processes being required for the removal of the contaminating elements.

A method due to E. Sebba and W. Pugh[2] has been successfully tested on a fairly large scale by A. R. Powell[3]. In this method sodium thiogermanate obtained by treating the mineral with a concentrated solution of sodium hydroxide is separated from other

sulphides by extracting with hot water. Arsenious sulphide and gallium, as sodium galli-arsenate $NaH_2Ga(AsO_4)_2.1{\cdot}5H_2O$, are separated leaving the germanium in solution. The germanium is eventually precipitated as germanium dioxide with ammonia. The precipitate is converted to the tetrachloride with hydrochloric acid and a crude germanium tetrachloride is obtained by distillation.

Tri-State Sulphide Ores

In the American zinc process[4], the sulphides in the Tri-State ore (Missouri, Kansas and Oklahoma) are first converted to oxides by roasting (see *Figure 1*). When these oxides are sintered with sodium chloride the germanium, together with cadmium and some other metals, is volatilized as the chloride and the vapours are condensed. Lead is removed from the resulting fume as lead sulphate after leaching with sulphuric acid. Addition of zinc dust precipitates germanium, copper, arsenic and some other metals, but cadmium remains in solution and is recovered subsequently.

The process is repeated until a suitable germanium concentrate is obtained. After roasting, the concentrate is dissolved in hydrochloric acid; germanium tetrachloride, arsenic trichloride and some hydrochloric acid are distilled off. This is rectified to give a crude germanium tetrachloride.

Figure 2. Solution of the regulus from the smelting process—by courtesy of Johnson Matthey

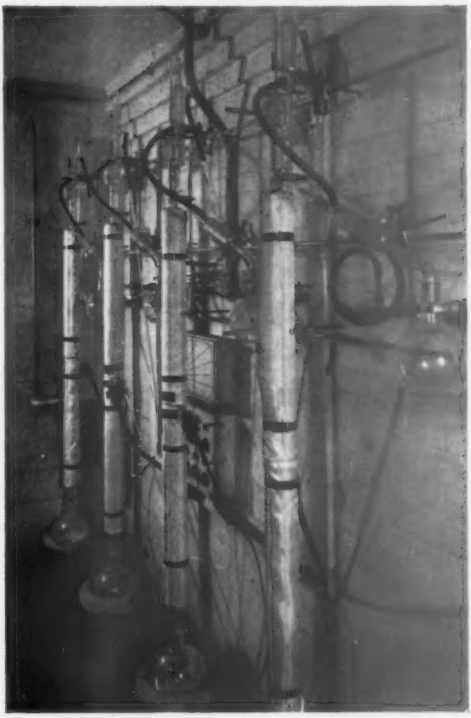


Figure 3. Fractionating columns for the purification of germanium tetrachloride—by courtesy of Johnson Matthey

The final stage of the American process makes use of the fact that concentrated hydrochloric acid and germanium tetrachloride are not miscible, and any arsenic trichloride present in the germanium tetrachloride is oxidized to the pentavalent state in the presence of chlorine and passes to the aqueous hydrochloric acid phase. The aqueous phase is easily separated from the volatile germanium tetrachloride by distillation and the arsenic remains in the constant boiling hydrochloric acid.

Recovery from Flue Dust

G. T. MORGAN and G. R. DAVIES[5] at the Chemical Research Laboratory at Teddington, showed that the germanium compounds present in some coals are volatile and become concentrated in the condensates formed in cool parts of the system in gas works. A. R. POWELL[3] has described the process used to obtain germanium from these flue dusts, a process which is worked commercially only in the United

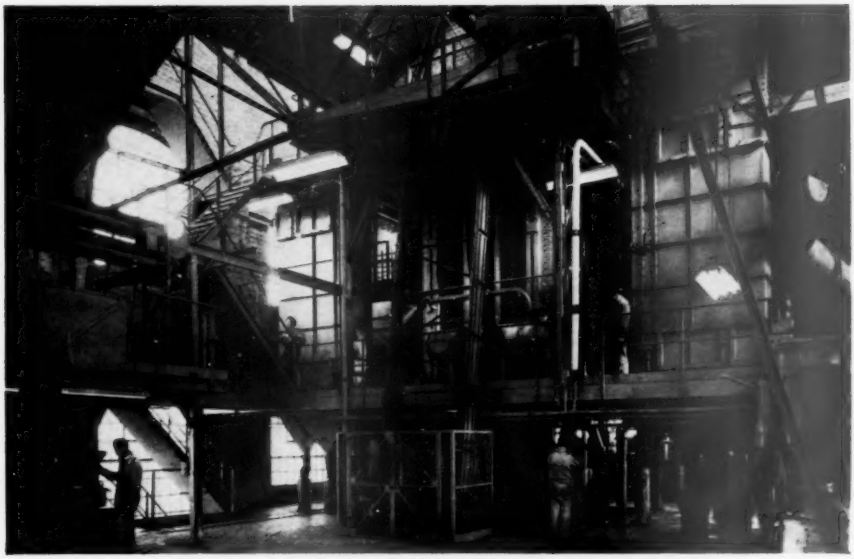


Figure 4. Vertical retort—reproduced from L'Onde Electrique *37 (1957) 701 by courtesy of the Editor and the Société Générale Métallurgique de Hoboken*

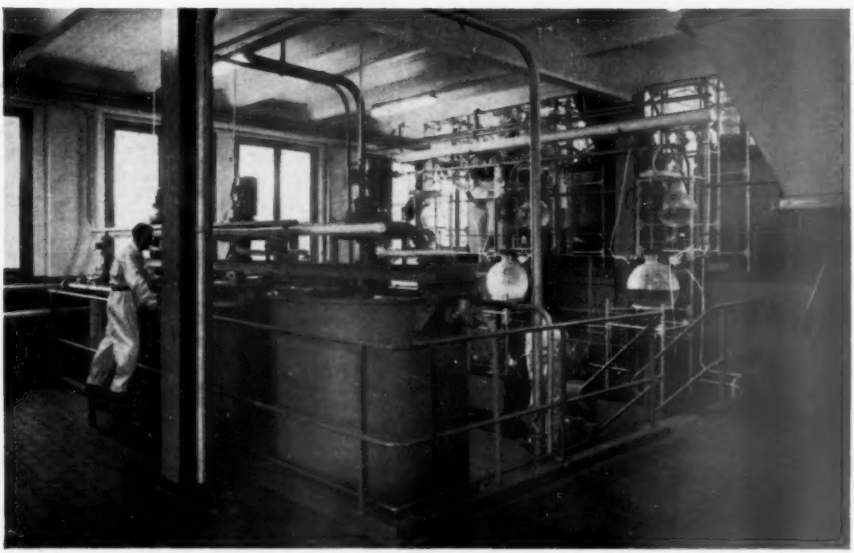


Figure 5. Neutralization tanks and distillation apparatus—reproduced from L'Onde Electrique *37 (1957) 701 by courtesy of the Editor and the Société Générale Métallurgique de Hoboken*

Kingdom. Another valuable constituent, gallium, is also recovered.

The dust is smelted with lime, soda ash, copper oxide and coal dust. Iron oxide present in the dust and the added copper oxide are reduced by the coal dust and the resulting iron and copper act as collectors for germanium and gallium respectively. The lime and soda ash act as fluxes for the non-reducible oxides and the product obtained is a regulus containing mainly copper, iron, germanium, gallium and arsenic. The regulus is treated with chlorine under a layer of ferric chloride solution to obtain the chlorides, the ferric chloride acting as a catalyst for the chlorination (*Figure 2*). Sulphuric acid is now added to react with some of the chlorides to produce sufficient hydrochloric acid to raise its concentration in the still to seven Normal. The volatile chlorides are distilled off. The gallium remains in the solution in the still pot. A two-phase distillate is obtained, the lower one being a crude germanium tetrachloride containing up to 20 per cent arsenic trichloride.

The crude germanium tetrachloride is purified by fractional distillation. In the first stage of the British process the tetrachloride is distilled through an adiabatic column held at 84°C and arsenic is reduced in the final stage by a long refluxing through a column packed with clean copper turnings. The apparatus is shown in *Figure 3*. Copper arsenide is formed, as in the Reinsch test, by the reaction of copper with arsenic trichloride.

Germanium Ores Found in Africa

The copper–lead–zinc sulphide ore found at Tsumeb, South-West Africa, contains germanite and renierite, but as they are finely dispersed, the ore has to be reduced to a very small particle size before separation by flotation becomes effective. In the first separation a zinc concentrate and a copper–lead concentrate are obtained. The latter is treated further to obtain a germanium concentrate which contains as much as 0·45 per cent germanium.

The deposits in the Belgian Congo are worked for copper and zinc. These are initially separated by selective flotation and the renierite containing the germanium accompanies the copper concentrate. This is converted to copper matte and finally blister copper. During these processes the germanium passes to the dusts which are carried away in the gases. The coarser particles are removed in a cyclone and the finer dust is collected in bag filters. This dust contains zinc, cadmium, 0·2 to 0·4 per cent germanium and about seven per cent arsenic.

These concentrates are processed at Olen in Belgium.

The Société Générale Métallurgique de Hoboken have developed a dry process for the recovery of the germanium from the African concentrates. In this process germanium and arsenic are volatilized by heating the pelleted concentrates in a reducing atmosphere in a vertical retort (*Figure 4*), the temperature

Figure 6. Hydrolysis of the purified germanium tetrachloride — reproduced from L'Onde Electrique *37 (1957) 701 by courtesy of the Editor and the Société Générale de Métallurgique de Hoboken*

being controlled to minimize the volatilization of lead sulphide. About 90 per cent of the germanium sulphide is volatilized in an atmosphere of hydrogen–carbon monoxide at 800°C, while only about five per cent of the lead sulphide is volatilized. The resulting vapours can be condensed or burnt directly in air, the oxides produced being collected in bag filters. The oxides are heated and the arsenious oxide volatilized off while the germanium remains behind. There are many problems in working the process and the solution of some of these is described in the paper by P. B. DE CLEENE[6].

The recovery of germanium exceeds 90 per cent. The oxidized residue contains 20 to 30 per cent of germanium dioxide, 30 to 50 per cent lead, 4 per cent arsenic and 2 per cent sulphur.

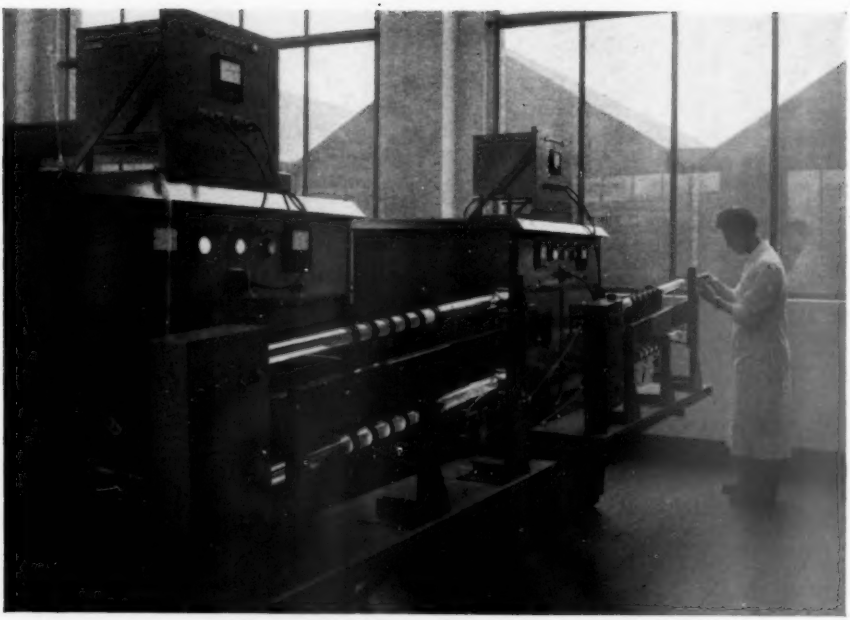


Figure 7. Equipment for zone refining—reproduced from L'Onde Electrique *37 (1957) 701 by courtesy of the Editor and the Société Générale Métallurgique de Hoboken*

The crude oxide is treated with concentrated hydrochloric acid, chlorine passed into the solution and crude germanium tetrachloride distilled in a current of chlorine gas (*Figure 5*).

Purification of $GeCl_4$

The tetrachloride obtained by the above processes may be hydrolyzed to give the oxide which can be reduced to the metal, but the purity of the product is not sufficient for semiconductor use. This arises because although the fractionation of the tetrachloride is efficient, the distillate is immediately contaminated by the materials of construction of the distillation equipment and by the water used for the hydrolysis. For instance, if the distillation apparatus is constructed from Pyrex borosilicate glass, there is a pick up of boron and arsenic.

This became apparent to several workers, especially in England, before the publication of the unequivocal demonstration of the efficiency of the distillation by M. GREEN and J. A. KAFALAS[7]. They carried out distillation studies on the germanium tetrachloride–arsenic trichloride system using radioactive arsenic 74 as a tracer in quartz and Pyrex distillation assemblies. In these tracer studies the arsenic 74 was removed by fractional distillation but absolute neutron activation analysis showed the presence of arsenic in the product from the Pyrex still, a result which could only be explained on the basis of contamination with arsenic from the glassware.

The purest germanium tetrachloride is obtained from fused quartz apparatus. Thus the method used for the purification of germanium tetrachloride of semiconductor purity is essentially that of L. M. DENNIS and E. B. JOHNSON[8], but conducted in a quartz apparatus. The process is conducted on a relatively small scale by some semiconductor device manufacturers and on a large scale at Hoboken. Besides eliminating arsenic, boron is also removed because of the low boiling point of its trichloride (12·5°C).

Preparation of GeO_2

Germanium dioxide is obtained from the purified germanium tetrachloride by hydrolysis with water which has been specially purified by ion-exchange or by multiple distillations from all-quartz stills. The hydrolysis has to be controlled because of the appreciable solubility of the oxide, the minimum solubility

being found when the concentration of the hydrochloric acid produced is five Normal. The oxide is filtered and dried.

Handling

The purity of the germanium tetrachloride and dioxide is such that extreme precautions have to be taken in handling the materials. The final processing rooms are air-conditioned with clean, filtered air. They are so designed that contamination does not arise from walls, paint or floors, *etc.* Special clothing is worn by the operators. The standards are as stringent as those in surgical operating theatres or in pharmaceutical laboratories for the production of vaccines and antibiotics. *Figure 6* shows the arrangements which are necessary at the hydrolysis stage.

Production of Intrinsic Germanium

The process for the reduction of the oxide is usually combined with that for the production of a normally frozen ingot, *i.e.*, one which has been solidified from one end.

The reduction is carried out at 650°C for some hours in a graphite or fused quartz boat. The graphite must be purified—for example by a high temperature chlorine treatment—since the purity required is superior to that used in atomic piles. At the end of the reduction the germanium is melted by raising the temperature to about 1,000°C. The molten germanium is slowly withdrawn from the furnace with the object of sweeping the impurities to the last liquid portion since they tend to remain in the liquid phase. The impure portion is removed by cropping before proceeding to the zone refining treatment. The normally frozen ingot has a resistivity of five to ten ohm cm.

The zone refining method has been described by its originator W. G. PFANN[9], and by C. H. L. GOODMAN[10]. Several molten zones are passed down an ingot of the metal and because of the higher solubility of most impurities in the liquid than in the solid, the impurities are effectively swept to one end. The product is intrinsic germanium with a resistivity approaching 50 ohm cm at room temperature. The content of electron accepting or donating elements in this material is such that the impurities make no significant contribution to the conductivity. An equipment for zone refining is shown in *Figure 7*.

The zone refined material is converted to monocrystals, after the controlled addition of the desired impurities, by the modified Czochralski technique[11] or the horizontal method[12]. Both lead to a final purification with respect to impurities which have favourable distribution coefficients between solid and liquid germanium.

Conclusion

The aim of all this chemical and physical purification is to give a product free from those impurities which have an adverse electrical effect. Most of these impurities, with the exception of boron, have a suitable segregation coefficient in zone refining. Boron segregates in the opposite direction from the others so that if boron is present the bar has to be cropped at both ends, with a resulting reduction of yield.

The chemical processes are important, therefore, since they effectively increase the yield from the zone refining process. It is also becoming clear that some elements are not removed by zone refining, so that the chemical purification process is important for reasons which will become more apparent as our knowledge of semiconducting materials becomes more complete.

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THE ELF SCREEN

A Flat Solid State Display Device

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IT IS becoming increasingly apparent that many modern imaging systems would greatly benefit from a new type of electrical to optical transducer which differs markedly from the conventional high vacuum display. This new imaging device should be capable of being constructed with a screen area that is many times that of a conventional cathode ray tube and it should have overall external dimensions which approximate to a thin panel. Among the important operational requirements for the improved display are high brightness, good resolution, fast scanning, accurately controlled halftones and flexible storage capabilities for minimum flicker.

Recent progress in the development of bright and efficient electroluminescent phosphors has encouraged attempts to build a solid state display screen. The back electrode on an electroluminescent panel can be composed of a plurality of separate isolated areas which define the 'elements' of the multielement display. A high resolution image can be formed on this electroluminescent panel if a carefully defined pattern of excitation is applied to these elements. The major problems to be solved lie primarily in the manner by which this excitation is distributed to and maintained on the screen.

An early suggestion was that an electroluminescent television display might consist of a phosphor sandwiched between an array of mutually perpendicular conducting strips in a matrix form. It was proposed that excitation be switched sequentially to the various rows and columns of the array in order to scan this screen. Careful study of the properties of intrinsic electroluminescence has shown that this approach is not feasible. Excitation must be applied simultaneously and continuously to the elements of an electroluminescent panel, rather than in short pulses, in order to achieve a bright, flicker free image. The process of providing this mode of a continuous excitation is here called storage.

One method of building storage into the electroluminescent screen is to incorporate a photoconductive structure which regulates the amount of excitation applied to the electroluminescent panel. Light feedback is permitted between the electroluminescent and photoconductive areas so that the elements of the screen function in a bistable manner. An image is formed by optically triggering various elements of the array from the dark to the lighted state. Some means must be associated with the screen in order to transform from an electrical video input to the optical triggering signals.

The photoconductive electroluminescent screen fails to meet the requirements set forth for the modern display device in that scanning speeds are severely limited by the sluggish response of the photoconductors. In addition, continuous halftones are not generally obtained since the elements are bistable or, at best, multistable. Finally, the elements, once they are triggered 'on' cannot be individually erased and power must be removed from a large section of the screen in order that new information may be applied.

A ferromagnetic control structure may also be used to apportion the excitation to the electroluminescent screen. There are several modes in which such a screen might be operated. The phenomenon of ferroresonance may be utilized in order that the elements be bistable. Alternately, the ferromagnetic structure may control the excitation applied to the electroluminescent elements in a continuous manner in accordance with control currents of fluxes established by a signal distribution system. In either case, the major disadvantage to this approach appears to be the physical realization of the control structure. The fabrication of 250,000 separate and non-interacting ten henry inductors on the back of an electroluminescent television screen would indeed appear to be a formidable problem.

A much more desirable means of building storage into the electroluminescent screen is to use ferroelectric control. The ferroelectric material is utilized for its non-linear capacitance characteristics.

The excitation applied to each point on the electroluminescent panel is determined by the capacitance of the associated portion of the ferroelectric control structure. This capacitance is, in turn, altered by a charge pattern distributed over the screen. Since the ferroelectric has a high dielectric resistivity the control charge pattern, and hence the image on the electroluminescent panel, remains constant until the pattern is purposely modified.

This type of solid state display, here called an ELF screen, offers simultaneous solutions to the problems of brightness control and storage. The ferroelectric layers are well matched in impedance to the electroluminescent layers and it is believed that large area, high resolution screens no more than a fraction of an inch thick can be fabricated by relatively simple electroding techniques. High contrast ratios and extremely flexible storage are obtained with moderate excitation requirements.

Ferroelectric Control

The ELF screen may be considered to be a configuration of electroluminescent and ferroelectric capacitors. *Figure 1* illustrates schematically one way in which they might be arranged in a multi-element array. In a more practical screen configuration, the 'elements' may actually be defined by the electrode configuration on a ferroelectric electroluminescent laminate and may be scarcely recognizable as separate entities. Regardless of the actual form of the screen however, the functions of the materials are always the same. The electroluminescent cell emits light in accordance with the a.c. potential appearing across it, while the ferroelectric body causes this potential to be altered in accordance with the applied video control potential.

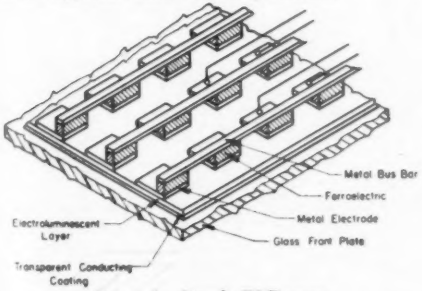

Figure 1., Simple ELF array

The electroluminescence utilized in the ELF screen is of the intrinsic type. Intrinsic electroluminescent cells generally consist of a phosphor powder embedded in an insulator and emit light only under the action of a changing electric field. Sustained emission does not result from application of a constant field nor does a constant field particularly affect the light output under alternating excitation. *Figure 2* illustrates the average brightness of a typical cell as a function of the amplitude of the applied voltage. It is important to note that the

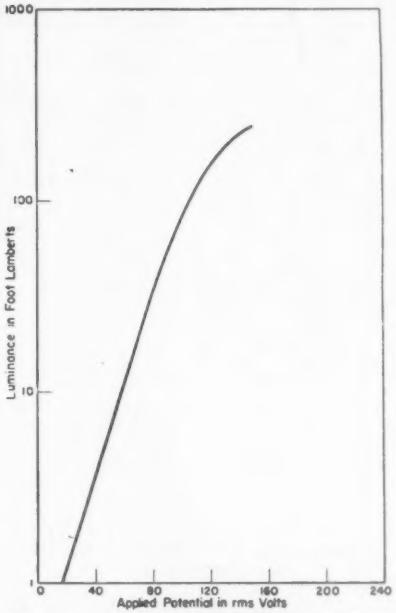

Figure 2. Brightness of a Westinghouse electroluminescent cell as a function of voltage

brightness varies very rapidly with voltage, changing by as much as 140/1 for a 5/1 change in excitation amplitude.

The ferroelectric used in the ELF screen is the ceramic form of barium strontium titanate. In this application, the property of this material which is of primary interest is its voltage sensitivity when used as a dielectric. Unlike ordinary capacitors whose capacitance is relatively independent of voltage, the effective capacitance of a ferroelectric is a function of the applied bias voltage or charge. *Figure 3* shows this behaviour for a typical unit. It should be emphasized that this curve illustrates the small signal behaviour of the ceramic and may not be used to compute the behaviour of circuits in which relatively large a.c. potentials are present. However, in qualitative considerations of circuit performance it is convenient to consider the ferroelectric capacitor as an element whose effective reactance increases with bias.

Although in the actual screen laminate it may be difficult to observe a specific circuit arrangement for each element, it is convenient to think in terms of an

equivalent circuit for the element in considering the operation of the screen. Actually, there are a number of different element configurations in which the ferroelectric components can exert the proper

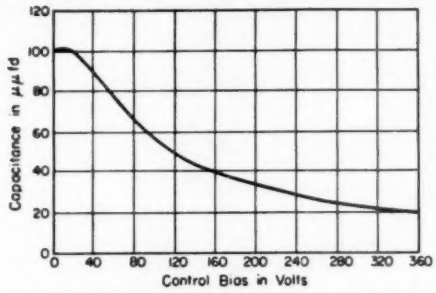

Figure 3. Small signal capacitance of a ferroelectric capacitor as a function of control bias

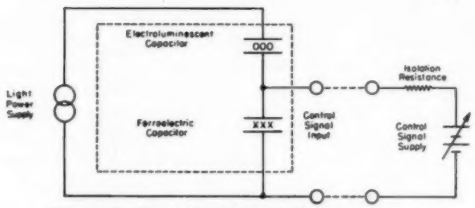

Figure 4. Equivalent circuit of the two component ELF element

influence on the excitation applied to the electroluminescent component. Each has certain advantages and disadvantages. The simplest arrangement is the series configuration of *Figure 4*. An electroluminescent and a ferroelectric capacitor are connected in series with an a.c. source which is called the light power supply. Typically this source might be 200 volts rms, 10,000 cps. In addition, provision is made for the introduction of a control potential. This is a undirectional charge or voltage which, for purposes of explanation, might be supplied by a battery in series with an isolation resistance.

Assume that the components in *Figure 4* are proportioned so that with no control potential applied, the a.c. potentials on the electroluminescent and ferroelectric cells are 150 and 50 volts respectively. This corresponds to the 'full-on' or bright condition for the element. If now the control potential is increased from zero, the capacitance of the ferroelectric body decreases. A larger fraction of the light power voltage appears across the ferroelectric and a smaller fraction across the electroluminescent cell. When the control potential reaches 500 volts d.c., the a.c. across the electroluminescent cell would be reduced to, perhaps, 50 volts. This is the 'off' or dark condition for the element.

From *Figure 2* it can be seen that dropping the excitation on the electroluminescent cell from 150 to 50 volts rms causes the brightness of the cell to diminish from 243 to 6·1 foot lamberts for a contrast ratio of nearly 40/1. As shown in *Figure 5*, the brightness can be set at any level in this range by the corresponding value of control potential or charge. If, after a control potential is established on the capacitors, the control supply is disconnected, the control charge is trapped and causes the element to continue to emit at the preset brightness level. This is the storage feature of the screen.

A three component ELF screen element is shown in *Figure 6*. In this circuit, the ferroelectric capacitors represent a larger fraction of the total a.c. loop impedance and therefore can exercise greater control over the excitation appearing across the electroluminescent cell. In addition, since the

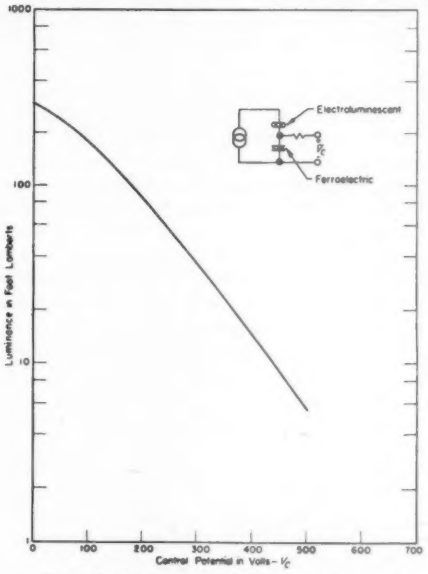

Figure 5. Control curve for a two component ELF element

control potential does not appear across the electroluminescent capacitor, the restrictions imposed by the relatively low breakdown strength of this component are considerably relaxed.

A bridge circuit element configuration is shown in *Figure 7*. The control potential is applied to the ferroelectric capacitors so as to cause the capacitance

of one to increase while the other decreases. This alters the unbalance of the bridge and varies the excitation applied to the electroluminescent cell. *Figure 8* shows a control curve for an experimental bridge configuration.

The dotted boxes in *Figures 4*, *6*, and *7* include the components which constitute an individual element of the multielement array. The isolation resistances, and the light power, bias and control signal supplies are usually common to the entire array. The actual arrangement of the components in a screen element may be varied markedly from that shown in the equivalent circuits in order to adapt the element to the electrical and mechanical constraints of the structure.

Using the three component and bridge configurations, model screens have been built which show contrast ratios of over 100/1 with control potentials as low as 200 volts. Typical highlight brightnesses for these screens are on the order of 25 foot lamberts and storage times of up to several minutes are common.

Screen Structure

The exact physical form of the ELF screen depends upon the element configuration and the details of the signal distribution system. A prime requirement of the structure, or course, is that the large number of elements which are required be formed by simple mechanized techniques.

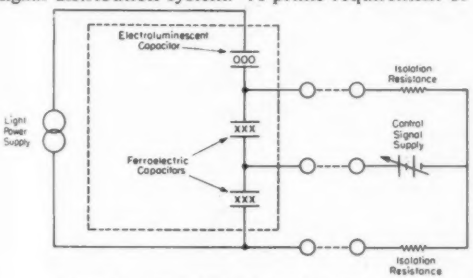

Figure 6. Equivalent circuit of a three component ELF element

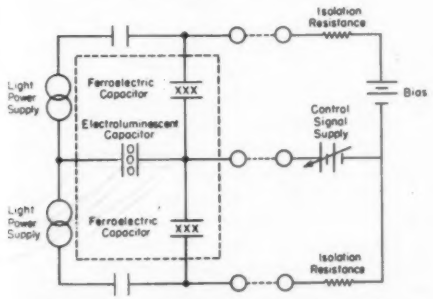

Figure 7. Equivalent circuit of a bridge configuration

A mosaic of separate electrodes may be applied to the back of an electroluminescent panel by

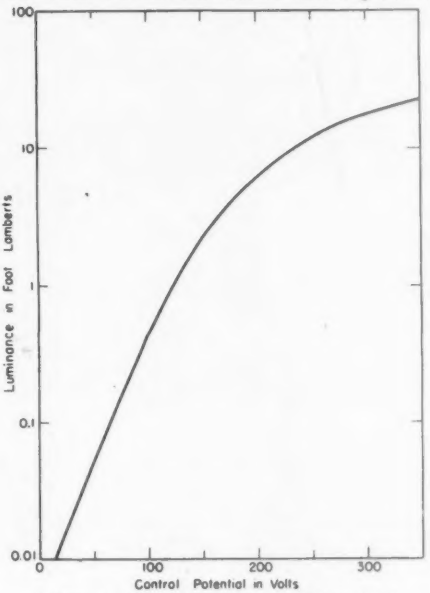

Figure 8. Control curve for a bridge ELF element

vacuum deposition of metal through a suitable mask. *Figure 9* shows a panel with a mosaic having 56 elements per inch; this by no means represents an upper limit. Excitation can be applied to any one of the electrodes without significant electrical or optical interaction with its neighbours.

There are a number of ways in which the ferroelectric structure can be provided. An early approach was to start with a metal–ferroelectric–metal sandwich as shown in *Figure 10(a)*. Special techniques have been developed by which sheets of brass may be intimately bonded to flat wafers of the ferroelectric ceramic. The composite slab is then slotted by a multiple cutter machining technique as shown in *Figures 10(b)* and *(c)* to form the control array which, in turn, is fastened to the electroded electroluminescent panel as shown in *Figure 11*. Each element of this ELF screen has the equivalent circuit form of *Figure 6*. The entire array is encapsulated to eliminate sparkover and increase mechanical stability.

A preferred method of construction is illustrated by *Figure 12*. The structure may be thought of as a

laminate of three separate layers. The first is the electroluminescent dielectric on which is deposited a mosaic of electrodes. Next, there is an insulating interface which contains a spaced array of conductors. The top layer of the laminate is a specially

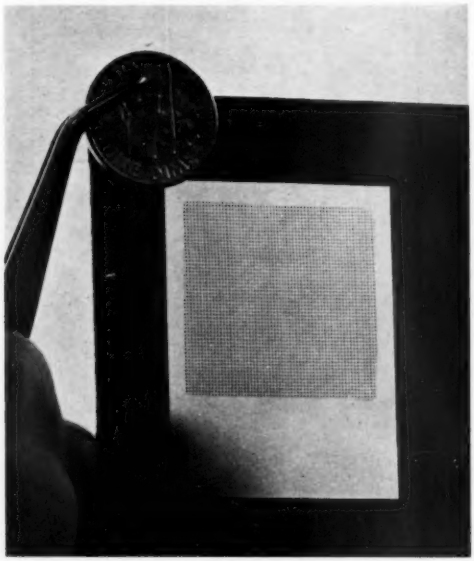

Figure 9. Electrode mosaic evaporated on an electroluminescent panel—56 elements/inch

electroded ferroelectric ceramic sheet. The control structure is formed by the electrode arrangement. *Figure 12* shows a laminate structure in which each element has the equivalent circuit of *Figure 6*. Similar laminates have been designed for other element configurations. A very desirable feature of this approach is that the conductors and many of the components required for the signal distribution system can be formed as an integral part of the screen structure.

With the cutting technique, screens have been built with from 4 to 10 elements per inch. The laminate approach should provide a significant increase in resolution.

Signal Distribution

The various methods for forming an image on an ELF display may be summarized in three broad catagories. The first is typified by the use of an electron beam to effect the generation of the control charge pattern. The second includes those approaches in which the distribution is accomplished by means of near-optical radiation. The third catagory includes systems in which the control charge pattern is established without direct recourse to electron scanning or optical means. For want of a more descriptive term, it is called ' ohmic '.

The screen may be scanned in a predetermined pattern or, the image may be constructed at random as information for various points becomes available. The latter case might be encountered where the image information comes from a computer. The ELF screen is excellent for such application because of its storage flexibility.

Ohmic Distribution

Present indications are that ohmic distribution will most closely satisfy dimensional restrictions imposed by the majority of the potential applications of the ELF display. Only one distribution system of this type will be described; however it should be emphasized that this system represents but one embodiment of a specific philosophy and there are many ohmic distribution philosophies.

Figure 13 shows the major components of a system for scanning an ELF screen in a predetermined pattern. It is assumed that the video is available on a single input bus and that appropriate to define lines and frames. The video information for one scanning line of the screen is first distributed to a set of intermediate storage cells. There is one intermediate storage cell for each element of a scanning line. Once the video has been arranged on the intermediate storage cells, the charge for an entire line is transferred en mass to the elements of that particular line.

Considering the operation in greater detail, the X pulse source in *Figure 13* supplies one synchronized pulse of proper shape to the X pulse distributor for each line of video information. This pulse distributor, which might be a delay line, carries this pulse to each of its outputs in rotation. When the pulse appears at a given output, it excites the associated X pulse actuated switch say, a diode, which closes momentarily to transfer the proper portion of the video line to the associated intermediate storage cell.

Once the X pulse has reached the last output of the distributor, charges which are indicative of the information in one video line have been stored in proper spacial accord on the intermediate storage cells which, in this case, could be capacitors. At this time, the Y pulse source and Y pulse distributor have cooperated to provide a pulse of proper waveform to the bus which traverses the line of the screen for which video information is now stored on the intermediate storage capacitors. This pulse causes the element pulse actuated switches for that

line to open simultaneously in order to transfer the control charge to the corresponding screen elements. The charges are deposited directly on the ferroelectric control capacitors or in an alternative approach they appear on a separate set of capacitors connected to the ferroelectric components by decoupling resistors.

The basic advantage of the intermediate storage philosophy is that the operating speed requirements on the element switches are greatly reduced. In a more practical system, the intermediate storage proceeds half a line at a time. Hence, a half line time rather than the scanning time for one element is available for transferring the control charges to the screen elements. More sophisticated embodiments are available in which several intermediate storage steps are included; these offer even greater relaxation of the speed requirements for the element switches.

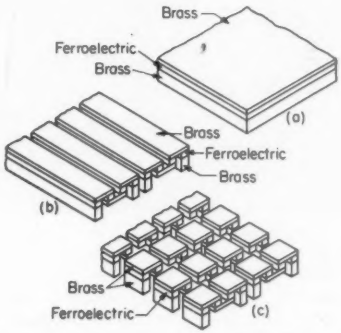

Figure 10. Formation of a ferroelectric control structure from a metal–ceramic–metal sandwich

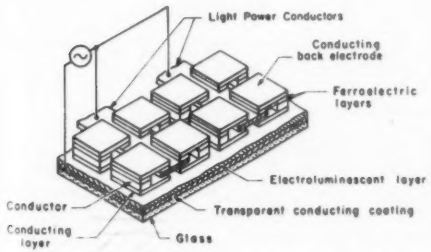

Figure 11. ELF screen structure using the control array of figure 10(c)

Electron Beam Distribution

This distribution approach takes advantage of the inherent ease of scanning of an electron beam. The ELF screen is incorporated in a cathode ray tube

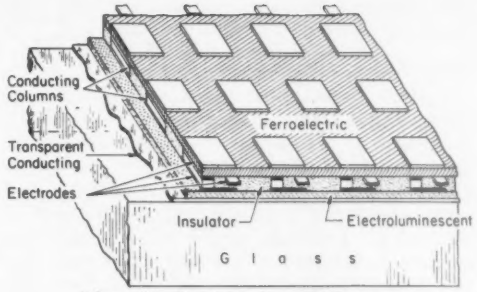

Figure 12. Laminate form ELF structure—ferroelectric insulating and electroluminescent material

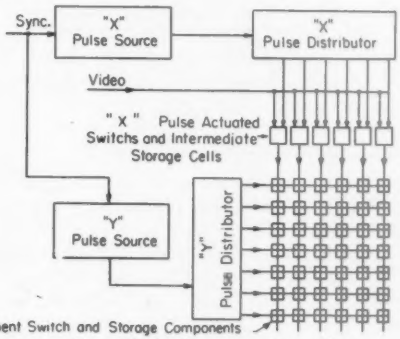

Figure 13. Block diagram of an ohmic distribution system

envelope as shown in *Figure 14*. A material having a secondary emission ratio greater than unity is deposited on the control electrodes and an electron collector screen is positioned behind the ELF array. If video is applied to the collector screen, the electron beam will bring each control electrode to the desired video potential as it scans the array.

There are a number of other ways in which the cathode ray beam can be used to distribute control signals. For example, the beam can scan solid state switches in which conductivity is induced by electron bombardment. These switches in turn commutate the video control signals to the ELF screen elements.

While distribution with an electron beam retains some of the disadvantages of the conventional cathode ray tube, it does provide a simple method for taking advantage of certain desirable features of the ELF array. The electron beam is relieved of the necessity of supplying the light power and instead acts only as a switching means. Consequently, the cathode ray tube accelerating voltage may be reduced. Since storage is inherent in the screen, a storage tube type of display can be achieved without

the shading difficulties associated with the more conventional tubes.

Optical Distribution

If a photoconductor is associated with each element of the ELF screen there results a device which is potentially a very desirable light amplifier. The photoconductor adjusts the amount of control charge on the ferroelectric capacitors in accordance with the input light. The ferroelectric capacitors, in turn, vary the intensity of the output light. This device differs from the conventional photoconductive-electroluminescent light amplifier in that the ferroelectric constitutes a ' gain stage ' between the input and the output, and the photoconductor is relieved of the task of carrying the power required to excite the electroluminescent material. As a result, the ELF light amplifier can have considerably greater gain than the conventional amplifier and it may make use of faster photoconductors that are required for the latter device.

Discussion

The principle of operation of the ELF screen is well established. Models have been built which show contrast ratios of over 100/1 with control potentials on the order of 200 volts. The highlight brightness for these models have been on the order of 25 foot lamberts. Storage times of several minutes are obtained under conditions of moderate humidity and there is reason to believe that improved encapsulation techniques will extend the storage period.

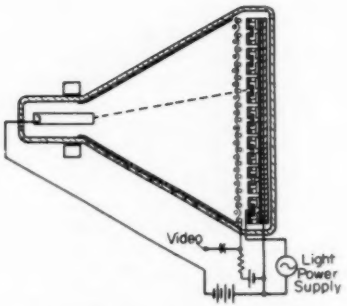

Figure 14. Electron beam distribution

Early experimental ELF models have had resolutions of four to ten elements per inch. Experience with improved fabrication techniques indicates that it should be possible to double these figures in the near future. Eventually, resolution of 50 to 100 elements per inch or more may be obtainable.

An ohmic distribution system has been tested and found to be quite feasible from a technical point of view. With this system, video information may be distributed to the screen elements at megacycle rates and it is believed that there is no technical barrier to the attainment of television scanning speeds.

Figure 15. Experimental model

Single element light amplifiers have been made in which photoconductors are used to set the control charge on the ELF elements. Tests show that these models have from 10 to 100 times the gain of straight photoconductive-electroluminescent amplifiers using the same photoconductive materials.

Conclusions

The ELF screen offers a fresh approach to the problem of large, flat screen imaging. By a very fortunate association of solid state materials it provides high brightness, continuous halftones, flexible storage and fast writing speeds. As is the case with almost every multielement display, the main technical problems are associated with economical screen fabrication and feasible signal distribution means. With the ELF screen, there is every reason to believe that these problems are surmountable.

MECHANICAL SEALS FOR ROTARY SHAFTS

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The lessons learnt in providing means of sealing rotary shafts under a wide range of operating conditions in the petroleum, chemical and other process industries have contributed knowledge of value to technicians throughout industry. To such readers this article is addressed, and its justification is that it can help to bring to their attention the capabilities and limitations of mechanical seals. Fundamental principles will be discussed by the progressive development of a definition of a mechanical seal.

THE PROGRESS that has been made in the design and manufacture of mechanical seals has been due, by and large, to the tremendous development and expansion within the petroleum, chemical and other process industries since the second World War. Other branches of industry, particularly the aircraft industry, have called for a distinctive contribution from the mechanical seal but the main incentive to development has come from the process industries. Solutions are demanded for sealing problems which range between extremes of shaft speed, pressure and temperature, and involve many chemical and physical problems such as corrosion and product stability.

The fundamental principles which will be discussed in this article are applicable in general to all types of mechanical seal and proprietary peculiarities of design have been avoided as far as is possible. There is, however, one apparent exception to this rule, which has been made in respect of the majority of illustrations, in order to achieve greater clarity. As will be explained later, it is necessary in any mechanical seal design to ensure that the 'sliding' seal ring either rotates with the shaft or remains stationary in a housing. This can be achieved in many ways, such as by the use of driving pins or lugs. It is simple for the purposes of illustration to assume that the spring which is invariably associated with the 'sliding' seal ring provides not only a closing force but also a torsional drive or constraint. Such an arrangement is in fact employed by more than one manufacturer but it is the exception rather than the rule.

Mechanical Seal

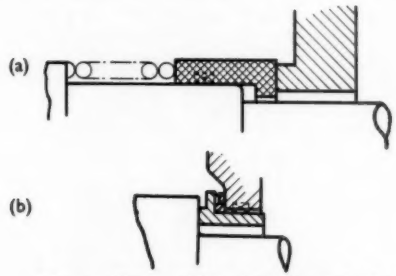
The term 'mechanical seal' requires to be defined in a manner that is not only logical but also corresponds with common usage. Firstly, the purpose of a mechanical seal is to enable a pressure difference to be maintained without significant leakage of the fluid concerned across a wall or solid barrier through which a rotary shaft must pass and function. In some sealing applications, such as those where grease or oil is being retained within a bearing, there is no pressure difference across the seal and the space has only to be closed against the spread of the liquid under the influence of gravity. The term 'closure' is commonly applied to such seals which may or may not otherwise have the characteristics of a mechanical seal.

The typical example of a sealing application for which a mechanical seal may be used is the sealing of a pump shaft where it passes through the stuffing box of a pump. Other devices which can be used for the same purpose are gland packing, lip seals, centrifugal seals and viscosity seals. It should be noted that the shaft to be sealed is one with rotary motion. Although small axial movements must often be tolerated, the sealing of a reciprocating shaft is not the function of a mechanical seal, and distinction is thus made from 'metallic packing'. This is the common term applied to that type of seal which uses predictable and controllable mechanical principles to seal a reciprocating shaft as does the mechanical seal on a rotary shaft.

Gland packing is a means of sealing both rotary and reciprocating shafts in a manner satisfactory for many applications but it lacks both predictability and controllability in more difficult circumstances. The main feature of both mechanical seals and metallic packing, which enables them to show a marked advance in these characteristics, is the use of substantially rigid sealing surfaces, this becoming the first tenet of a definition of a mechanical seal.

This requirement eliminates from consideration gland packing, lip seals and centrifugal seals, but still retains within the class the viscosity-type seal which in one form is a close clearance stationary bush about the shaft which permits a pressure to be built up across the annular space between the shaft and bush while allowing only a small and

acceptable leakage rate. The leakage may be reduced or eliminated by the use of a scroll on either surface, but this is only effective when the shaft is rotating. The surface and the bore of the bush must be considered as sealing surfaces, although



Figures 1(a) and (b). Simple mechanical seals according to definition

not in rubbing contact, since even in face type seals which have the rubbing faces in a plane at right angles to the axis of the shaft it can often be demonstrated (and more often argued) that a fluid film exists between the faces.

It is not, therefore, enough to specify that the faces must be in rubbing contact since this would take the definition out of the field of clear fact. Nor is it possible to eliminate the viscosity seal from the class by specifying the angle between the plane of the faces and the axis of the shaft, since viscosity seals need not necessarily be cylindrical in form, nor need face type seals have their faces at right angles to the shaft. Further, certain types of viscosity seal lie within the class of mechanical seals just as much as that type of mechanical seal in which a lubricant is forced between the rubbing faces and which could easily be placed outside the class by an unwisely stated definition.

The second essential tenet of a definition is that there should be some mechanical means of exerting a closing force between the faces. A definition can be stated accordingly as follows

> ' A mechanical seal is a device for sealing the annular space between a rotary shaft and a hole, in which two substantially rigid faces, one rotary and the other stationary, are forced towards rubbing contact by some mechanical means.'

Figures 1(a) and *1(b)* show two mechanical seal arrangements of which the heavy lines represent the requirements stated in this definition. In *1(a)* the means of applying the force, *viz.* a spring, is rotary; in *1(b)* it is stationary. It goes, of course, without saying that the design of a mechanical seal must enable it to function effectively, and the definition given implies but does not state certain further features which are essential to it and which can be derived from it.

Secondary Sealing Mechanism

Since a spring of some type is required to act through one of the sealing rings, this sealing ring must be capable of axial movement and cannot, therefore, be one with either the shaft or housing. This entails the provision of a sealing mechanism between the sealing ring and the shaft or housing (with whichever the sealing ring is associated) which must be able to tolerate the requisite axial movement. This movement will certainly be required as the seal faces wear, and may also be due to differential expansion or other axial movements imposed by the design of the apparatus on which the seal is fitted.

This secondary seal—the rubbing faces make the primary seal—may be either a sliding gasket or a diaphragm, the latter being commonly in the form of a bellows. The former is the more common among seals for onerous duties, and the broken lines in *Figure 1(a)* and *1(b)* extend accordingly the definition in respect of these two sealing arrangements by introducing the o-ring, or toroidal sealing ring according to British Standards, which is a simple but effective form of sliding gasket.

It will be realized that no mechanical seal could hope to accept even normal amounts of shaft vibration, eccentricity or swash if both sealing rings were

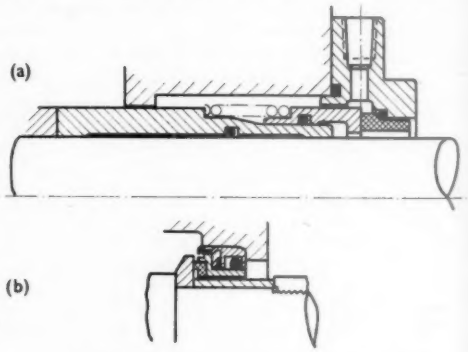


Figure 2. Mechanical seals according to a fully developed definition

rigidly mounted. The design of the secondary seal almost necessarily provides for the resilient mounting of the sliding sealing ring, and it is not fundamentally necessary for the mounting of the second sealing ring to be resilient. The definition does, therefore, cover this point, and it becomes a matter of detail design whether the second (or fixed) sealing ring is

rigidly or resiliently mounted. *Figures 2(a)* and *2(b)* show the arrangements of *Figures 1(a)* and *1(b)* in commercially acceptable forms; it will be noticed that in *2(a)* the stationary sealing ring is resiliently mounted while in *2(b)* the rotary sealing ring is rigidly mounted. These are the fixed sealing ring in each case.

Torsional Drive

A further essential feature of a mechanical seal is the torsional drive or constraint applied to the sliding sealing ring. This sealing ring, which is that through which the spring load is applied to keep the faces of the seal effectively in contact, may be either the rotary ring or the stationary ring, and must either be driven with the shaft or constrained against rotation. In some cases, and particularly in the case of cheap low duty seals, the interference of the sliding packing is relied upon to perform this function. *Figures 1(a)* and *1(b)* showed no more than such an arrangement but *Figure 2(a)* introduces the spring type of drive already mentioned while *2(b)* utilizes two lugs in the outer cup, which engage in slots in the stationary seal ring, to restrain it from rotation. The main requirement of any form of drive is that it should be achieved without disturbing the squareness of the sliding sealing ring.

Transmission of Load

The spring means employed in a seal may consist of either one helical spring concentric with the shaft, a multiplicity of smaller springs spaced evenly around the shaft or one or more spring washers of various types. *Figure 2(a)* shows a seal with one helical spring while *2(b)* shows a seal employing a wave type spring washer. While the use of a number of small springs in place of the one concentric spring is quite common on all sizes of shaft, there is a greater tendency towards their use for larger diameters. Where the spring means is in contact with a corrosive product the use of one spring, of comparatively large gauge, is preferable for its likelihood of greater endurance.

The load required, to be transmitted to the seal faces by the spring, is that which will keep the faces in effective sealing contact when the pressure differential across the seal is nil. The only exception to this is in the case of a seal where the intended pressure differential is such as tends to open the seal faces; and in this case the spring must be capable of withstanding a stated 'blow-out' force. This exception becomes the rule where products under vacuum have to be sealed, and a common criterion of spring load for general purpose seals, which have to withstand either pressure or vacuum conditions, is that the spring load should be capable of withstanding the 'blow-in' force due to atmospheric pressure when the product is under full vacuum. This criterion often produces a spring load which is greater than is required, to overcome the friction of the sliding packing and the effects of normal vibration and misalignment. For specialist applications the spring load of a general purpose seal may well be reduced if problems of heat dissipation are likely to arise.

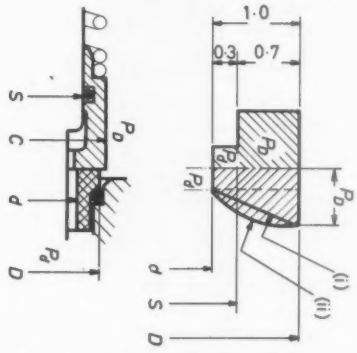


Figure 3. Diagramatic representation of the balance of a typical mechanical seal

The Sliding Packing

The sliding packing, which may be either the rotary or the stationary seal ring packing, is a vital component of a seal and material selection is of extreme importance. The most suitable materials are natural or synthetic rubbers and other resilient plastics. These may be used in the form of o-rings, chevrons, bellows and other less common forms. Good mechanical properties, and in particular good compression set characteristics, are desirable, but these have sometimes to be compromized to obtain satisfactory chemical or temperature resistance. Fortunately, most of the types of resilient materials are being continually improved in their detail properties, and new materials are being developed. For example, the silicone rubbers have shown considerable improvements in mechanical properties and the newer fluorosilicones and Vitons have opened up fresh fields of application.

As has been mentioned in the previous paragraph, the frictional drag of the sliding packing must sometimes be carefully related to the spring load, and the aim of detail design is to produce a packing with predictable behaviour in this respect. The use of resilient materials makes such design comparatively simple, but the frequent necessity to use a chemically resistant plastic material, such as PTFE, creates greater difficulty.

'Balance' of Seals

The most important design feature of mechanical seals is that usually referred to as 'balance'. This expression denotes the relationship of the sliding diameter to the inside and outside diameters of the sealing face area. It determines how the pressures being sealed affect the axial equilibrium of the

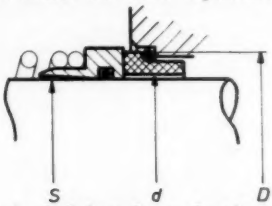


Figure 4. Unbalanced type of mechanical seal

sliding sealing ring. This equilibrium involves four systems of force

(*i*) the load of the spring or springs;

(*ii*) the resultant force of pressure acting between the sliding diameter and the outer rubbing face diameter;

(*iii*) the resultant force of pressure acting between the sliding diameter and the inner rubbing face diameter; and

(*iv*) the resultant force of the pressure system between the rubbing faces.

The full analysis of the balance of a seal must take all these forces into account in order to arrive at the closing force. This is the excess of the resultant of all forces and pressures, other than the face pressure, over the resultant force of the fluid pressure system, if any, across the rubbing faces.

Whilst a detailed analysis is sometimes required, it is more often only necessary to classify a seal according to the balance made between its sliding diameter and the outer and inner diameters of the rubbing face area. If the sliding diameter is equal to the mean of the face diameters, the average total face pressure will equal the mean of the two pressures being separated, plus the pressure due to the spring load. As the sliding diameter is varied in relation to the face contact area, so the face pressure becomes more or less determined by either of the pressures being separated. This relationship is vital to all design calculations, whether it be to determine power absorption or to design a seal suitable for widely alternating or reversing pressures. A simple means of expressing this relationship should replace the different forms of expression currently in use.

The balance of a seal is purely geometrical and its expression should be in geometrical form. The balance of a seal is the same whether it faces one direction or the other; the reversal of the seal does not alter its nature nor should it be held to alter its balance. According to most customary modes of expression, the reversal of a seal alters its balance since the balance is expressed in terms of that one of the pressures being separated, which is supposed to be the governing pressure. These systems fall down completely when a complex seal arrangement is under discussion, since no agreement can be presupposed as to which is the governing pressure.

'Balance' Expressed in Geometrical Form

In order to formulate a means of expression of 'balance' in purely geometrical terms it is felt necessary to adopt the term 'balance ratio' instead of 'balance', and to relate it always to the position of the spring means. Accordingly, the following definition is advanced

> 'The balance ratio of a mechanical seal is the ratio p/P, where P is the pressure in the space in which the spring means is situated, and p is the component of the total face pressure due to P.'

The pressure p will be negative if the pressure in the spring space tends to open the seal faces.

This definition can be stated in purely geometrical terms but the use of the concept of pressures—which is in any case completely relevant—simplifies the matter considerably. In the case of a bellows, care has to be taken in the determination of the sliding diameter which controls the balance ratio. Distinction has to be made between those parts of the bellows which are substantially rigid and parts which are substantially flexible and which will transmit the axial component of pressure to the seal face.

Balanced and Unbalanced Seals

Figures 1(a), 2(a) and *3* represent seals with a balance ratio of approximately 0·7, a proportion widely used in seals for process pump duties. According to the definition above the relevant pressure space, that in which the spring is situated, is that which contacts the outside diameter of the face area; the pressure in this space is p_D. Accordingly the balance ratio equals

$$(D^2-S^2)/(D^2-d^2)$$

since it will be appreciated that the pressure acting between the diameters C and D has no axial resultant. In *Figure 4* the same expression represents the balance ratio, which in this case will have a value somewhat in excess of unity. These seals are generally called balanced and unbalanced seals respectively. The first seal, which may variously be called 70 per cent or 30 per cent balanced, is represented in the catalogues of most seal manufacturers; one manufacturer at least has a seal with a balance ratio of 0·9 which is designated, with equal legitimacy, a balanced pressure seal. The

'unbalanced' seals of different manufacturers vary quite widely in their precise balance ratio. Some have a ratio of 1·0 precisely, while the majority show the effect of the clearance between the shaft and the inner diameter of the rubbing face area by having a balance ratio in excess of unity.

It must be agreed that the expression 'balance ratio' does not lend itself well to the generalized description of seals though it will be shown later that it permits very precise verbal specifications to be made. One popular form of expression which fits in well with the use of balance ratios has as its datum seal that which has a balance ratio of zero. This is described as 'completely balanced' while a seal with a balance ratio of 0·7 is 70 per cent out of balance and a seal with a ratio of 1·2 is 120 per cent out of balance. This system is easy to use though it has the demerit that the datum seal is a rarity in practical use.

The seal shown in *Figure 5* can be precisely described as follows

> 'A mechanical seal of 0·3 balance ratio having a rigidly mounted rotary sealing ring and a stationary sealing ring with o-ring type packing sliding within a housing. The seal separates the product being handled by a pump from atmosphere, the spring being situated in the atmosphere.'

This seal is 30 per cent out of balance relative to the atmosphere but 70 per cent out of balance relative to the product space. It is, therefore, fundamentally similar to the seal in *Figure 3* which was also 70 per cent out of balance, although it is both reversed and inside out. The essential fact differentiating between the two seals is the position of the spring.

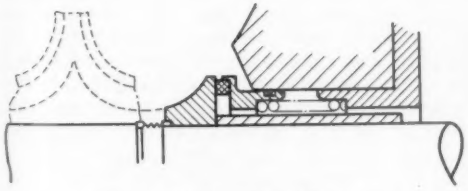


Figure 5. Mechanical seal fitted to a centrifugal pump

Returning to the question of balance it is necessary to discuss further its effect. Firstly, it is clear that the face pressure can be varied within wide limits when a high pressure is being sealed from a low pressure. In the type of seal shown in *Figure 3* a liquid pressure $p_D = 100$ p.s.i. being sealed from atmosphere at 15 p.s.i.a. approximately, will produce a mean total face pressure of

$$(0{\cdot}7 \times 100) + (0{\cdot}3 \times 15) + 15 = 90 \text{ p.s.i.}$$

if 15 p.s.i. spring pressure is being applied.

In the type of seal shown in *Figure 4* the same pressures will produce a mean total face pressure of

$$(1{\cdot}1 \times 100) - (0{\cdot}1 \times 15) + 15 = 124 \text{ p.s.i.}$$

In either case it may be assumed for the sake of

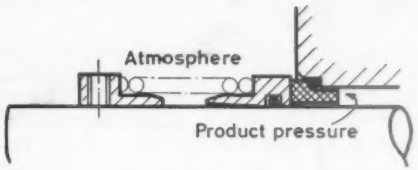


Figure 6. Externally fitted mechanical seal

the present argument that the product will tend to leak across the seal faces with a straight line pressure drop (line (i) in *Figure 3*) so that the mean fluid pressure between the faces will be

$$15 + 0{\cdot}5\,(100 - 15) = 57 \text{ p.s.i.}$$

On this basis the closing pressures of the two seals are $90 - 57 = 33$ p.s.i.
and $124 - 57 = 67$ p.s.i.
In a similar fashion these two seals separating 1000 p.s.i.a. liquid pressure from atmosphere would give closing pressure of 203 and 607 p.s.i.

If, however, it is assumed that the product between the faces vapourizes due to a high rubbing face temperature, then the pressure drop across the faces may be expected to be parabolic (line (ii) in *Figure 3*). In the sealing of 1000 p.s.i. the mean fluid pressure between the faces will be 672 p.s.i.a. and the closing pressures of the balanced and unbalanced seals become 38 and 442 p.s.i.

Face Pressure Conditions

These figures have been given to assist consideration of the problems determined by the conditions existing between the faces of a mechanical seal. They imply that the liquid product being sealed is present between the faces and that it has a certain pressure distribution from outside to inside diameter of the rubbing faces and that there is also solid contact between the faces. This is quite conceivable since the theoretical thickness of the film of a light product leaking between two surfaces of perfect flatness and surface finish may well be less than the actual deviation from such perfection on the part of a pair of actual rubbing faces. In such circumstances the power absorption of the seal will consist of a component due to the solid contact and a component due to the shearing of the product layer between the faces. The viscosity and stability of the product and the balance of the seal will determine the relative importance of the two components.

It is quite conceivable with a comparatively viscous product either that in the one extreme there is no

solid contact or that in the other extreme there is no liquid penetration between the faces at all and the contact is entirely solid. The latter circumstance has been demonstrated under both laboratory and field conditions. With less viscous products it is far less likely that such extremes would occur and, in the case of products which vapourize under the pressures and temperature conditions between the faces, the closing pressure determined, in a fashion similar to the above calculations, will be by far the more significant factor than the fluid layer in the development of torque and thence of power absorption. The pressure distribution within the fluid layer will, of course, be important in determining the closing pressure and the figures quoted above show how considerable is its influence.

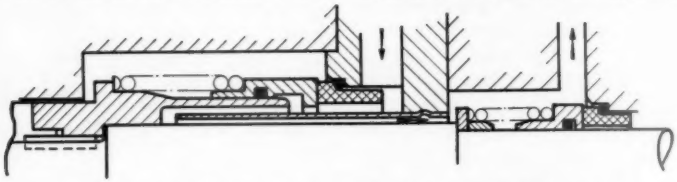


Figure 7. Double mechanical seal for high pressure applications

The fundamentals of this problem are not understood completely though several opinions have been published largely unsupported by experimental evidence. It is known that research work is in progress on this problem in several establishments. The essential factor, in the empirical solution of the problem, is the determination of torques and the construction of a test-rig which permits the accurate determination of the torque, under substantially practical operating conditions, poses a number of design problems of which a satisfactory solution is difficult to achieve. The construction and operation of such equipment has not yet been the subject of any published data.

Limiting Conditions for Operation of Mechanical Seals

It is often necessary to quote a figure which will determine the maximum conditions under which a seal will operate reliably. The statement of chemical and temperature conditions is simple enough and the mechanical limit is usually given as a *PV* factor. This factor is only comparative when applied to seals of similar balance and general design, particularly in respect of features which may determine the heat transfer capacity of the surface of the seal which is in contact with the liquid being sealed. If it is accepted that the principal criterion of seal performance is face temperature then this will be a function of heat development and heat transfer. The surface area available for the transfer of heat is usually approximately proportional to the square of the seal diameter and the dimensions of the expression for face temperature become foot pounds per minute divided by square feet. Expressed differently as pounds per square inch multiplied by feet per minute; this corresponds to the *PV* factor which is the product of the pressure being sealed and the surface rubbing speed. It is not correct to use the face pressure as a component of the *PV* factor since this is a largely indeterminate property. Its use would encourage the comparison of different designs of seal according to *PV* factors and such comparison is not valid.

Common Design Practice

The general design practise of most seal manufacturers has followed a similar pattern and most seals for high pressure duties utilize a balance ratio of 0·65 to 0·75. This approximates to the minimum balance ratio at which stable equilibrium of the sliding seal ring is maintained if the fluid pressure drop across the faces assumes a parabolic form. Practical experience supports the validity of this assumption where the viscosity of the product is low.

Seals for lower pressures use much higher balance ratios. Where circumstances permit a ratio of unity or even a balanced construction is employed, but in the majority of cases the ratio is in excess of unity. The design practise in respect to low pressure seals varies far more widely than that for high pressure seals since the operating conditions vary so much. The seal which is to act as a closure for the viscous lubricant of a high speed bearing, with little or no pressure difference across the seal, is a different design proposition to the seal of a small water pump operating against 50 foot head at 1450 rev/min. The overriding characteristic of low pressure seals is, however, that they conform to their surroundings as readily as possible without imposing conditions which would make for unnecessary expense.

Arrangement of Seals

More important to the user than the detail design of seals are their possible arrangements and combinations. There are two fundamental arrangements of single seal; that in which the pressure difference tends to close the seal and that in which it tends to

open the seal. There are likewise two fundamental arrangements of double seal unit according to the type of inner seal. Where the pressure between the seals tends to close the inner seal this pressure must be maintained higher then the pressure within and the outer seal may, therefore, need to be designed for high pressure operation. Where, however, the pressure inboard of the inner seal tends to close that seal, the circulation pressure between the seals may be low and the outer seal may be designed accordingly. Sets of three or more seals may be encountered but are not common.

The commonest and most useful arrangement of a single seal for use against a liquid product is that in which the spring is in the product space and the balance ratio varies between 0·7 and 1·1. The lower balance ratio is used for medium and high pressures and the larger ratios are used mainly for reasons of economy of construction for pressures up to 50 or 100 psig at normal speeds of 2900 or 1450 rev/min.

Frequently it is desirable to keep the spring or springs out of the product and sometimes it is more economical to fit a seal in this way. *Figure 6* shows a single seal with a balance ratio of 1·1, the spring being in the atmosphere space. Normal methods of expressing operating limits are thrown to the wind in these cases since an increase in pressure results in a decrease of face pressure. Conversely, a product under vacuum increases the loading on the seal. These remarks do not apply to all externally fitted seals, for as in the case of the seal shown in *Figure 5* they can be balanced so that the product pressure tends to close the seal faces. An important point to note in seals of this type is that when the sliding seal ring is constructed of more than one component in such a way that pressure can penetrate between the constituent components, then there is a possibility of the seal being unstable quite apart from its balance. More than one commercial design is strictly limited in respect of external fitting for this reason.

Combination of Two Seals

A combination of two seals is useful for the sealing of gas and in certain other circumstances. Only very limited *PV* values can be accepted under dry running conditions unless a complex form of facet type gas viscosity seal is employed and it is usual to circulate a liquid between two seals in order to provide cooling. This permits much higher *PV* values to be withstood, particularly if the liquid pressure is made higher than the gas pressure. This demonstrates most forcibly the advantage of liquid penetration between the faces, though it can also be a cause of embarrassment where even the slightest contamination of the gas is impossible.

Where the gas pressure is higher than the liquid pressure it is most important for the heat generated at the faces to be transferred to the liquid or along a continuous metal path of good conductivity as effectively as possible. *Figure 7* shows a double seal arrangement designed with this in mind. The liquid circulation makes far more effective contact with the seal rings of the inner seal than in most simpler seal arrangements and in addition the resilient o-ring seals are well protected against excessive temperatures when the gas is hot.

This seal arrangement in *Figure 7* is designed in order to cope with high gas pressures without the liquid pressure being more than nominal. This is evidenced by the balance of the inner seal and by the fact that the outer seal is unbalanced. This type of seal is also employed for the sealing of hot liquids at high pressures such as boiler feed water. *Figure 8* shows a double seal which requires that where the gas pressure is above about 30 p.s.i. the liquid pressure between the seals must match the gas pressure by being at least almost equal to it. This is often impracticable, but the simplicity of the arrangement commends itself for many less onerous duties.

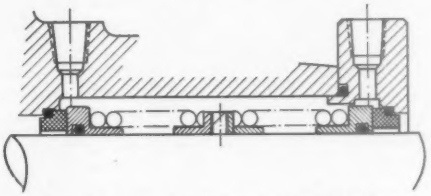


Figure 8. Double mechanical seal for low pressure applications

This type of seal in *Figure 8* is used not only for gas sealing but also for the sealing of abrasive products or for fluids which have some objectionable property which makes it desirable that there should be the minimum possible contact with the seal components. Some clean or otherwise acceptable liquid is circulated between the seals.

Finally, to close this article, it should be emphasized that a seal is an essential part of the equipment to which it is fitted. The success of the machine is often as dependant on the efficiency of the seal as on its essential performance. For this reason the requirements of a seal to cope reliably with the relevant duty should be studied for their incorporation in the general arrangement of the machine.

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SUGAR DETERGENTS

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Barnes, London, S.W.13

A new class of synthetic detergent, based on sucrose esters, is likely to become available shortly for general washing and other purposes. The author describes the development of these detergents and compares some of their physical and chemical properties with those of products which are in current use. The adoption of the new materials on a large scale may help to solve certain difficulties which have occurred in the treatment of sewage.

IT WAS announced recently that a new class of synthetic detergents, in which the active ingredients are relatively simple derivatives of sucrose, is soon to become commercially available[1]. These sugar detergents were developed in America by Foster D. Snell Inc. and by the Sugar Research Foundation, and are being manufactured in the United Kingdom by Howards of Ilford Ltd, Essex (see *Figure 1*) and by Glovers Chemicals, Leeds. The hope has been expressed that sugar detergents may not only prove to be competitive with those based on more conventional surface active agents, but may also possess the advantage of greater susceptibility towards degradation by microorganisms, thereby helping to solve the problem[2,3] of how to remove detergents from sewage and waste water before they are finally discharged into rivers and streams.

Sucrose Esters

The active ingredients of sugar detergents are certain fatty acid esters of sucrose and an early reference to the attempted preparation of such compounds dates back to 1860 when M. Berthelot tried unsuccessfully to produce the stearic acid ester by heating sucrose with stearic acid[4]. In 1918, S. Oden prepared the pure octacinnamoyl sucrose[5] and in 1921 K. Hess[6] obtained octastearoyl sucrose by reacting sucrose with stearoyl chloride in quinoline. The potential of allyl sucrose as a material for protective coatings and as an adhesive was put forward[7] in 1923, and patents[8] for the preparation of the stearic acid esters of sucrose which involved heating equimolecular quantities of sucrose and of stearoyl chloride in a pyridine solution were taken out in 1933.

Sucrose Octaesters

Systematic work on the preparation of sucrose esters by the Sugar Research Foundation started after the last war and M. ZIEF[9,10] has described the preparation of fifteen octa substituted esters by treating sucrose with the appropriate anhydride or acid chloride in pyridine. The general reaction with the acid chloride is as shown in *Figure 2* and some physical properties of the esters prepared by Zief are listed in *Table 1*.

Owing to their ability to polymerize and form cross linked network structures the octa substituted esters have useful potentialities as protective coatings and their use in this field is extending. They have been proposed as water repellents[11] and as plasticizing agents in non-aqueous systems, but as their solubility in water is low they themselves do not exhibit surface active characteristics. It is not in fact until the degree of substitution in their molecules is considerably reduced that marked surface activity develops; most strongly by the mono- and disubstituted esters and to a lesser extent by the tribsubstituted esters. It is on these that the new detergents are to be based.

Monoesters and Diesters of Sucrose

The preparation of a number of mono- and diesters of sucrose has been described[12]. The preferred method for the monoesters involves dissolving one mole of sucrose in about one litre of dimethyl formamide by heating with vigorous stirring. One third of a mole of the methyl ester of the appropriate fatty acid and about one twentieth mole of potassium carbonate are added—the latter acting as a catalyst—and the solution is maintained at 90° to 95°C and 80 to 100 mm mercury pressure for twelve hours. The dimethyl formamide is then distilled off under vacuum. Analysis of the reaction mixture after various periods of time shows that the following steps occur. The methyl ester first reacts rapidly with the sucrose to form the mono- and diesters in about equimolecular amounts. On further heating the diester reacts with more sucrose and reverts to the monoester. Thus after three hours the ratio of mono- to diester is about 1: 1, after six hours about 2:1 and after twelve hours about 24:1.

In theory 255 different esters (including isomers) could be formed in a single run. Although preliminary work[13] has indicated that monosubstitution occurs predominantly in the '6' position, as indicated in *Figure 3*, this has not been confirmed

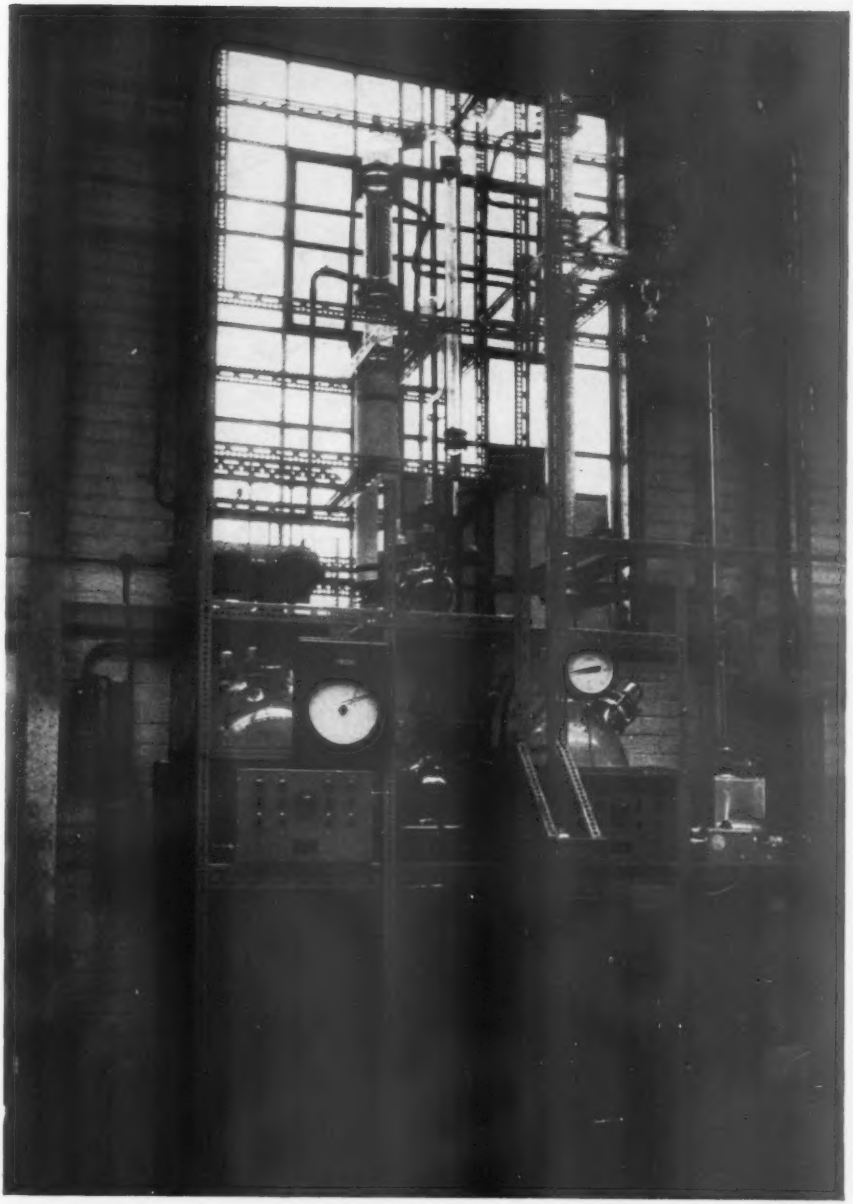

Figure 1. Pilot plant for the preparation of sucrose esters (by courtesy of Howards of Ilford Ltd)

and the exact configuration of the product is still under investigation.

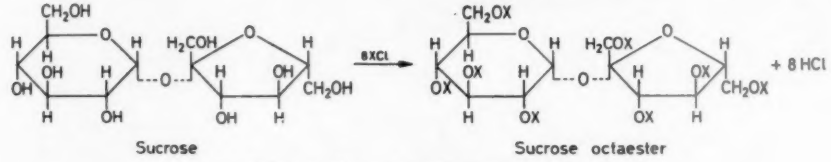

Figure 2. Formation of sucrose octaester

The product of the reaction contains about 54 per cent sucrose and about 45 per cent of sucrose ester. To obtain the ester in purer form the material is partitioned between butanol and an aqueous salt solution, the ester dissolves in the butanol from which it is recovered by distillation under vacuum.

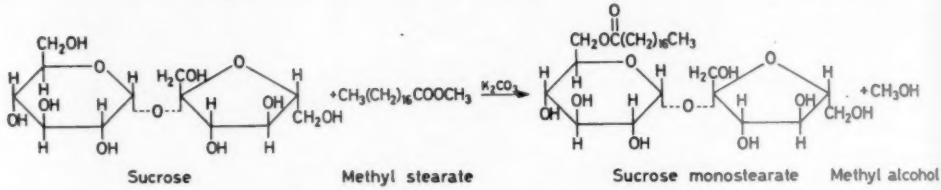

Figure 3. Formation of sucrose monostearate

The procedure for the preparation of the sucrose diesters is essentially the same as for the monoesters, except that the ratio (in moles) of sucrose to methyl ester of the appropriate fatty acid is now 1:2 instead of 3:1. After distilling off the methanol and dimethyl formamide the diester is recovered better than 90 per cent pure.

Detergent Properties

A certain amount of work has been published on the physical chemistry of the sucrose monoesters and this includes their surface chemistry[14] and an evaluation of their detergent properties[15].

Like other water soluble surface active agents, the sucrose monoesters form micelles in solution[16] and critical micelle concentrations (molar, at 25°C) are compared below with those of certain other surface active agents.

Sucrose monolaurate	3×10^{-4}
Sucrose monostearate	6×10^{-6}
Sodium dodecyl sulphate	6×10^{-3}
Sodium cetyl sulphate	4×10^{-4}
Potassium laurate	2×10^{-2}

Addition of salts, amines, alcohols *etc* to the solutions reduces the critical micelle concentrations and this is in accord with expectation.

The surface and interfacial tensions of five monoesters of sucrose are given in *Table 2* together with their wetting properties, as measured by the time taken for a weighted skein of cotton to sink when placed in a 0·2 per cent aqueous solution of the ester[17] at 50°C. The cotton, which is unscoured, is normally covered with a thin layer of grease, which retards wetting and keeps air trapped in the pores of the material. In the presence of a wetting agent, however, the grease is displaced; water penetrates into the material displacing air, and this reduces the buoyancy. Thus the greater the efficiency of the wetting agent the shorter the time taken to sink.

Table 3 gives the results of tests carried out to measure the ability of the esters, after suitable building up with other chemicals, to remove dirt from soiled cotton and also to prevent dirt being deposited on to clean cotton from dirty water. The composition (wt.%) of the built detergents was

Surface active agent	20
Sodium tripolyphosphate	40
Tetrasodium pyrophosphate	10
Sodium metasilicate	10
Sodium sulphate	10
Sodium bisulphate	10

which corresponds roughly with that of a typical domestic detergent powder[18]. The results in *Table 3* are expressed as units of brightness regained; a positive value indicates that cleaning has taken place, a negative value that dirt has been deposited on the material.

The foaming characteristics of the built detergents are given in *Table 4* in terms of the amount of foam produced by a standard method of generation[19] and the rate at which the foam collapses when it is allowed to stand for various periods of time.

The conclusions to be drawn from these studies is that, as far as wetting properties are concerned,

the monosucrose esters compare favourably with other surface active agents. In general they reduce the interfacial tension between water and Nujol more than a condensation product of Tall oil and polyoxyethylene, which may be regarded as a representative non-ionic surface active agent, but are less effective than a typical anionic surface active agent such as sodium dodecyl benzene sulphonate.

In their ability to remove dirt from soiled cotton, they compare favourably, after building, with two typical detergent formulations, but they are somewhat inferior to the non-ionic polyoxyethylene condensate in preventing soil redeposition. (This could probably be overcome by adding sodium carboxy methyl cellulose, which is currently employed for the purpose in domestic detergent powders).

The amount of foam produced by the monoesters varies from moderate (laurate and myristate) to low (palmitate and stearate) and this is clearly likely to be an advantage in circumstances where foam is undesirable.

The emulsifying powers of the esters are excellent. The mono-, di- and triesters can all be dispersed in water and they are soluble in alcohol, organic solvents, vegetable and mineral oils, particularly when these are warmed. They produce oil in water emulsions when present in low concentrations (one to three per cent); at higher concentrations (three to ten per cent) they favour the formation of water in oil emulsions, particularly if used in conjunction with auxiliary emulsifiers such as glycerol monostearate or esters of sorbitol and mannitol (*e.g.*, Spans, manufactured by the Atlas Powder Co.).

The stability of the emulsions is good and a number designed for cosmetic purposes have been subjected to ageing tests with satisfactory results.

Table 1. Physical properties of some octaesters[9]

Group X		*Physical appearance*	α_D^{25}	η_D^{25}
(A) SATURATED OCTAESTERS				
Propionyl	$(CH_3CH_2CO–)$	syrup	+51·8	1·4588
Butyryl	$(CH_3(CH_2)_2CO–)$	syrup	+46·0	1·4550
Caproyl	$(CH_3(CH_2)_4CO–)$	syrup	+33·4	1·4582
Caprylyl	$(CH_3(CH_2)_6CO–)$	syrup	+26·7	1·4615
Capryl	$(CH_3(CH_2)_8CO–)$	syrup	+19·7	1·4677
Lauroyl	$(CH_3(CH_2)_{10}CO–)$	semi-solid	+20·7	1·4683
Myristoyl	$(CH_3(CH_2)_{12}CO–)$	powder, m.p. 41–42°	+18·0	—
Palmitoyl	$(CH_3(CH_2)_{14}CO–)$	powder, m.p. 52–53°	+17·4	—
Stearoyl	$(CH_3(CH_2)_{16}CO–)$	powder, m.p. 60–61°	+16·9	—
(B) UNSATURATED OCTAESTERS				
Methacrylyl	$(CH_2{:}CCH_3CO–)$	liquid	+30·8	1·4847
Crotonyl	$(CH_3CH{:}CHCO–)$	syrup	+39·3	1·4980
Cinnamoyl	$(C_6H_5CH{:}CHCO–)$	powder, m.p. 84–86°	+11·6	—
Furoyl	$(OCH{:}CHCH{:}CCO–)$	powder, m.p. 90–99°	+48·2	—
Undecylenoyl	$(CH_3(CH_2)_7CH{:}CHCO–)$	liquid	+21·0	1·4720
Allyl oxy-carbonyl	$(CH_2{:}CHCH_2–OCO–)$	liquid	+39·6	1·4778

Table 2. Surface and interfacial tensions and wetting properties[15]*—soft water is 36 p.p.m. and hard water 264 p.p.m of calcium carbonate*

	S.T. (dynes/cm)* CONCENTRATION (%)			*I.F.T.* (dynes/cm)† CONCENTRATION (%)			*Sinking time* (sec)	
	1·0	0·1	0·05	1·0	0·1	0·05	*Soft water*	*Hard water*
Sucrose laurate	33·4	33·7	35·6	7·6	7·9	8·4	33	37
Sucrose myristate	33·1	34·8	34·8	7·3	7·0	7·4	52	46
Sucrose palmitate	33·7	33·7	35·0	6·3	6·2	6·2	41	48
Sucrose oleate	31·8	31·5	32·7	5·4	5·0	6·2	25	48
Sucrose stearate	33·5	34·0	33·7	6·2	7·7	7·2	97	112
Tall oil–polyoxyethylene	40·4	41·0	42·0	6·7	7·2	7·7	62	33
Sodium dodecyl benzene sulphonate	31·0	29·4	29·3	2·3	2·0	2·6	1	1

* Aqueous solutions at room temperature † Against Nujol

A representative formulation (wt.%) for a hand lotion is

Stearic acid	7·0
Lanolin	0·5
Sorbitol	5·0
Sucrose stearate or distearate	3·2
Water plus perfume and preservative	84·3

and others are given for foundation cream, shaving cream, cold cream, and cleansing cream[20].

There are two particular characteristics of the sucrose esters, toxicity and stability toward microorganisms, which have been investigated and which may be discussed appropriately at this point.

Toxicity

The first concerns their effects on human and other organisms. Do they, in fact, have any toxic qualities if ingested and are they likely to produce irritation, dermatitis, *etc* if used as ingredients of detergent and cosmetic preparations ? The answer to this question on the basis of data so far published would seem to be no.

Tests carried out on rats[15] showed that no harmful effects were produced when ten per cent of sucrose monostearate was added to their diet for a period of one month. Single doses of 5g of sucrose stearate per kilogram of body weight introduced through a stomach tube likewise had no effect.

Other tests[20] have indicated that no irritation is produced when preparations containing ten per cent of sucrose stearate are applied to the eyes, while intravenous injections of aqueous solutions have not produced redness or swelling. Although these findings must be considered preliminary, they are as one would expect from the chemistry of the materials. Hydrolysis by enzymes or other body fluids splits the esters into sucrose and the appropriate fatty acid and these are not only innocuous, but may be utilized by the body as food. It is for these reasons that the sucrose esters are likely to be of particular value as dispersing agents and emulsifying agents in the manufacture and processing of food, in pharmaceuticals, detergents and cosmetics.

Stability towards Microorganisms

An important point about the sucrose esters is that, on the basis of preliminary reports at least[21], they appear to be more susceptible to attack by microorganisms than alkyl sulphates, alkyl aryl sulphonates and other surface active agents that are currently employed in domestic detergent products.

Table 3. Soil removal and deposition[15]—deposition on clean cloth with 0·025 per cent added carbon black; soft water is 36 p.p.m. and hard water 264 p.p.m. calcium carbonate

	Soil removal				*Soil deposition*			
	Soft water		*Hard water*		*Soft water*		*Hard water*	
	Concentration (%)				Concentration (%)			
	0·35	0·2	0·35	0·2	0·35	0·2	0·35	0·2
Sucrose laurate	11·1	12·0	12·3	9·6	−30·1	−28·6	−31·0	−33·3
Sucrose myristate	11·3	12·3	13·8	14·9	−29·1	−27·2	−38·9	−31·0
Sucrose palmitate	12·9	13·4	15·5	15·3	−26·1	−25·5	−32·7	−31·6
Sucrose oleate	12·5	12·8	16·3	12·1	−27·1	−26·0	−35·4	−31·6
Sucrose stearate	12·1	12·9	14·1	11·1	−28·1	−21·6	−29·0	−29·3
Tall oil–polyoxyethylene	12·5	10·9	11·0	8·9	−12·9	−18·7	−15·0	−29·9
Sodium dodecyl benzene sulphonate	12·9	13·3	14·2	10·5	−35·3	−28·3	−36·7	−31·8
Water	3·0	2·9	4·0	3·1	−44·7	−44·3	−42·6	−40·8

Table 4. Foaming tests on 0·2 per cent built detergent[15] at 43°C—soft water is 36 p.p.m. and hard water 264 p.p.m. of calcium carbonate

	Foam height (in cm)					
	Soft water			*Hard water*		
	Time (in min)			Time (in min)		
	0	1	10	0	1	10
Sucrose laurate	13·0	12·5	12·0	9·5	9·0	2·5
Sucrose myristate	14·0	13·5	12·0	8·0	7·0	6·0
Sucrose palmitate	1·5	1·0	1·0	0·5	—	—
Sucrose oleate	8·0	7·5	7·0	2·0	2·0	1·5
Sucrose stearate	1·0	0·5	—	0·5	—	—
Tall oil–polyoxyethylene	2·0	2·0	1·5	2·5	2·0	2·0
Sodium dodecyl benzene sulphonate	20·0	18·0	18·0	22·0	19·5	19·0

The widespread use of synthetic detergents by industry and by the public has caused difficulties in sewage works which rely very largely on bacterial degradation for removing organic impurities from waste water[23]. Conventional surface active agents

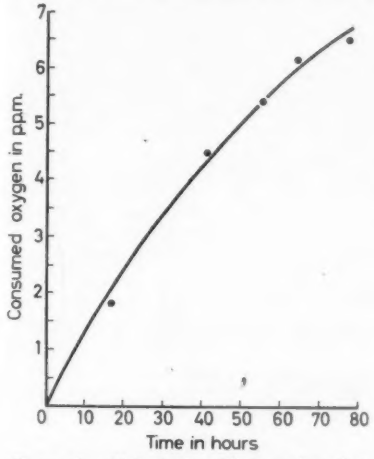

Figure 4. Biological oxidation of surface active agents—the consumed oxygen is due to the presence of 10 p.p.m. Sequol-260. (The graph is reproduced from figures kindly supplied by Dr P. C. G. Isaac)

not only interfere with sewage processing, but pass more or less unchanged through the plant and may thus escape into rivers and streams into which the final effluent is discharged. The net result is that the rivers tend to become polluted with incompletely degraded organic waste products, while the liberated surface active agents cause foam, particularly in the neighbourhood of locks and weirs[2,23].

In order to assess the susceptibility of sucrose esters to biological oxidation, P. C. G. Isaac and D. Jenkins[24] of the department of Civil Engineering at King's College in the University of Durham have measured the rate at which sequol-260 (a sucrose ester of cottonseed oil) is oxidised in a biological process (*Figure 4*) and compared the results with those obtained for a typical alkyl aryl sulphonate. For the purpose sewage, taken from the Felling U.D.C. sewage works, was diluted with aerated water and the rate at which it absorbed oxygen measured. The difference in p.p.m. between the amount of oxygen absorbed by the sewage seeded water alone and the sewage seeded water with detergent present was plotted against time, and some typical results are given.

Clearly the greater the susceptibility of the detergent to oxidation the higher the curve, for any particular concentration of detergent, and on this basis the sucrose ester is much more susceptible than alkyl aryl sulphonates. These results are preliminary and further experiments are planned. But there seems no reason to doubt that similar results will be obtained with other sucrose esters.

Conclusion

Sucrose esters can now be bought in this country[20] but a number of problems remain to be solved before they can be expected to appear as ingredients of domestic detergents. Some of these are technical; for example the fact that the sucrose esters are susceptible to attack by microorganisms makes them inherently less stable than, say, alkyl aryl sulphonates and this will necessitate incorporation of suitable stabilizers and preservatives in any industrial and domestic formulations.

Again, in domestic detergents it is necessary to blend numerous ingredients with the surface active agent to obtain products suitable for general use[18,25]. A good deal of work remains to be done on the blending and formulation of detergents based on sucrose esters and this, in turn, is likely to require modifications to existing manufacturing plant, or even the design and installation of completely new plant.

Competitive Prices

The price of the new detergents is likely to be an important consideration, especially since the recent findings[26,27] that certain modified alkyl aryl sulphonates, like the sucrose esters, may also be more susceptible to attack by microorganisms than existing types.

Sucrose esters, at the moment, are somewhat more expensive, than alkyl aryl sulphonates. However, the raw materials from which they are made—sucrose and natural fats—are both reasonably cheap and as improved methods of production are evolved there is every reason to envisage that the price of the esters will fall. Moreover, since the surface active agent only accounts for about one-fifth of the total weight of a typical detergent formulation and the cost of the ingredients is, anyway, only a proportion of the total cost of the manufactured product, it is reasonable to predict that, in due course, sugar detergents will appear on the domestic market.

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ESSAY COMPETITION FOR SCHOOLS AND TECHNICAL COLLEGES

RESEARCH in conjunction with TECHNOLOGY is this year organizing the third essay competition for schools. Because of the interest shown in the earlier competitions and the quality of some of the entries TECHNOLOGY has agreed to join RESEARCH in sponsoring the competition and extending its scope to include both pupils from technical colleges and secondary modern schools. The essays will again be judged for content, clarity of presentation and style but account will also be taken, particularly in Section I, of the type of course the entrant is following.

Prizes of £15 will be awarded for the best entry and £10 for the next best entry in Sections I and II; prizes to the same value will also be presented to the school or college library of the prize-winners. In Section III there will be a first prize of £30 and a second prize of £20. In each case the prizes may take the form of books or instruments.

Section I

A report, about 800 words long, on any piece of practical work or project in biology, chemistry or physics written by a schoolboy or girl whose *sixteenth birthday falls on or before June 1st, 1959.*

Section II

A report, about 1000 to 1500 words long, on any piece of practical work or project in biology, chemistry or physics written by a schoolboy or girl *over the age of sixteen on June 1st, 1959.*

Section III

A critical essay of about 1000 to 1500 words on which of the new metals promises to be most useful to technology. This section is open to any student attending a technical college who is *under the age of twenty-one on June 1st, 1959.*

The competition is only open to technical college students under the age of twenty-one or to pupils receiving full-time education at school. Entries will be accepted after June 1st, 1959 and the final closing date is July 31st, 1959. Please write for full details to The Editor, RESEARCH, *4 and 5 Bell Yard, London, W.C.2.*

THE SHORTEST RADIO WAVES

Scientists have experimented for many years with electromagnetic waves and it is very surprising that there is one portion of the vast spectrum which has remained largely unexplored. This is the region between the infra-red or heat waves and microwaves, the very short waves used in radar. The wavelength range of this gap in the spectrum is from 0·1 mm to 5 mm.

As a communication band this has an attractive feature—its bandwidth (3×10^{12} c/s) is about 100 times the total bandwidth used today for all television and sound broadcasts, radio links and radar. Since the amount of information conveyed is proportional to bandwidth this means that at present only one per cent of the channels ideally available are being used. From a physicist's viewpoint also there is considerable interest. At slightly longer wavelengths, the interaction of microwaves with matter especially in paramagnetic salts and semiconductors has led to fundamental discoveries in atomic and nuclear physics. At shorter wavelengths, infra-red spectroscopy is a well established chemical technique that has been of considerable importance in the study of molecules. It is desirable that these studies should be extended and unified.

Few experiments have been made in this waveband simply because suitable generators and detectors are extremely hard to make. Valve techniques fail because of the small size of the resonant structures and the high circuit losses. One method of generating very short wavelengths is by radiation from a deflected electron. This has the advantage of radiating into space without any need of a resonant circuit.

When an electron is deflected by an electric or magnetic field or by a collision, the resultant acceleration gives rise to radiant energy. The radiation is obtained at the expense of the kinetic energy of the electron, which is slowed down, usually by a small amount. This is a well known result in the Lorentz theory of electrons. An electron that is accelerated once will emit a small amount of energy during the time of its acceleration. Such a single pulse can be shown by Fourier analysis to be equivalent to energy spread very thinly over a large wavelength band. To get radiation power concentrated in a narrow band it is necessary to deflect the electron in a periodic manner. In the magnetic undulator (see *Figure 1*) the deflection is accomplished by a spacially periodic magnetic field. At first sight it might seem that the radiation should have the same 'wavelength' as the magnetic field. Provided however that the electron velocity is within a few per cent of that of light two scientific phenomena can be exploited to make a structure of reasonable physical size generate very short waves. The first is the relativistic Fitzgerald contraction which causes the magnet separation to appear shorter in the electron's

Figure 1. Basic arrangement of the magnetic undulator

frame of reference. The second is the Doppler effect whereby an observer with the beam approaching him sees an even shorter wavelength than the contracted magnet separation. Thus emitted radiation has a very short wavelength; for example with an electron accelerated through 2 million electron volts the reduction factor is 50. In the undulator experiments so far performed the magnetic field period was 4 cm which thus should give radiation at 0·8 mm. In fact power at sub-millimetre wavelengths was detected at Stanford[1] and in work recently started at Oxford millimetre wave power has been observed in a preliminary experiment.

In these experiments we are concerned not with single electrons but with bunches of a million or more which are generated by a linear accelerator. It is apparent that the length of each bunch must be short compared with a wavelength; for if a bunch were a half wavelength long power radiated from its front end would cancel that from the rear. Even with adequately short bunches the undulator is inherently inefficient, since if an appreciable fraction of the electron's kinetic energy is given up as radiation, it will slow down and the radiated wavelength will increase. However to achieve short bunches seems to be a very difficult technical rather than fundamental problem. With a linear accelerator to produce the fast electrons, peak beam powers—the product of beam voltage and peak beam current—of a few kilowatts are easily obtained. Hence even allowing for the low efficiency there is no basic reason why peak powers of the order of watts should not be obtained eventually. An undulator of this description would be very adequate for a scientific survey of the properties of this gap in the spectrum.

D. WALSH

[1] MOTZ, H. *Trans. Inst. Radio Engrs* AP4 (July, 1956) 374

SURVEY

The Production of Uranium Fuel Elements

At the end of January, almost exactly ten years after the delivery of the first consignment of pitchblende ore, the Springfield uranium processing plant was opened to the press and to foreign visitors for the first time. Visitors were shown both the old and the new production plants. The old plant was originally used to produce uranium from pitchblende for the military programme and for the experimental reactors at Harwell. The new plant, which has been built at a cost of about £12 million, will be fully commissioned in about a year's time and when completed should meet the needs of the eight reactors at Calder Hall and Chapelcross and also of the civil nuclear power stations. Sir WILLIAM COOK, the Member of the U.K.A.E.A. responsible for engineering production, stressed the fact that if export contracts were obtained, the necessary expansion to the Springfield plant could be accomplished much more quickly than the building of the corresponding power stations.

The extraction processes in the old and new plants differ slightly although the basic principles remain the same. In the first case the use of pitchblende entails some radiation hazard—on opening the barrels radon gas will escape from the ore—and therefore the ore must be crushed and the uranium extracted with a mixture of nitric and sulphuric acids using as little manual handling as possible. Uranium is then precipitated from the resulting uranyl nitrate solution with hydrogen peroxide. The precipitate, uranium peroxide, is hydrolized and metallic impurities are removed by extracting the uranium salts with ether; the latter is a solvent which most engineers prefer not to use.

In the new plant, however, uranium is extracted from oxide concentrates containing about 80 per cent uranium received as such from the Commonwealth countries and the process is therefore correspondingly simpler. The concentrates are dissolved in dilute nitric acid—this also, of course, dissolves other metallic impurities—and silica and insoluble materials filtered off. The uranium is then extracted continuously with a solvent, tributyl phosphate, which is specific for uranyl ions and is only slightly inflammable. Pure uranyl nitrate is reprecipitated by the addition of water.

At present the pure uranyl nitrate undergoes a complex conversion process in the old plant, for this section of the new plant has not yet been completed. The nitrate is precipitated as ammonium diuranate by the addition of ammonium hydroxide. The diuranate is filtered off and placed in an electric furnace where it is converted first to the trioxide at 350°C, then to the dioxide by reduction with hydrogen at 700°C and, finally, to the tetrafluoride by treatment with hydrogen fluoride gas at 450°C. In the new plant the ammonium diuranate stage will be eliminated, the nitrate solution will be heated and decomposed to give the solid trioxide.

Uranium tetrafluoride, a turquoise powder, is used as the starting material in the final extraction. It is mixed with magnesium turnings and compressed into pellets which are stacked in a stainless steel crucible and heated to about 950°C. The fluoride is reduced and pure uranium metal —a purity of 99 per cent or better is claimed— which collects at the bottom of the crucible in the form of a billet weighing about 200 kg. (Formerly the more expensive calcium metal was used instead of magnesium.)

The billets and any clean scrap are melted (1400° to 1600°C) in a vacuum furnace by high frequency induction heating. The vacuum appears not to be very critical, for no argon flush is used and the degree of vacuum needed is only about 5 mm Hg. The furnaces each have a capacity of 500 to 550 kg and eight furnaces are available for simultaneous operation. The molten metal is poured into graphite moulds coated with sprayed alumina which are placed at the bottom of the vacuum furnaces. On cooling the rods or tubes, are removed from the mould, straightened and subjected to standard metallurgical heat treatments. Fuel rods, such as used at Calder Hall, are about three feet long and one inch in diameter.

During this entire process sampling is carried out in order to ensure that the purity of the final uranium rod is of the order of 99·98 per cent. (The impurities present usually absorb neutrons and would diminish the efficiency of the power stations considerably.) In order to prevent surface wrinkling of the fuel elements in the pile, they are subjected to what is termed a ' beta quench treatment '. The rods, or tubes, are passed through a high frequency induction heating coil to convert the metal to the beta phase and quenched in water to produce the required fine grain size. The rods are subsequently annealed, cleaned and the ends machined. Concentric small grooves are also machined at 6 in. intervals; these help to give a tight fit between rod and can at a later

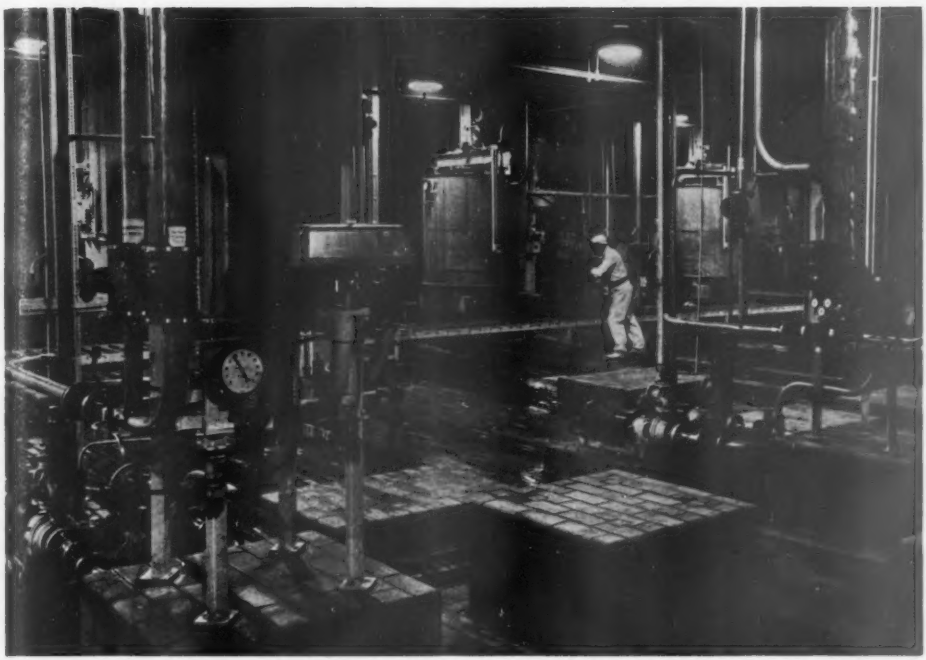

Figure 1. New uranium processing plant at Springfields. Underneath the deck carrying the primary dissolvers and filters, the various necessary intermediate stages are performed. In this picture the operator is removing a drum of the insoluble sludge taken from the primary filters

stage. The fuel elements are, of course, weighed and checked for length. All swarf is collected and it is claimed that more than 99·8 per cent of the total uranium is utilized.

The fabrication of the fuel elements is perhaps the most intricate part of the whole process. The uranium rods are inserted into extruded and rolled Magnox cans through a hole in a partition, for only on one side of the partition are bare fuel rods allowed to be handled in order to prevent contamination of the surface of the can with uranium metal. The ends are then welded on to the can, the system evacuated and a small amount of helium is injected. The whole assembly is then ' pressurized ' using oil at 200° to 250°C and 10,000 lb/in² pressure; this treatment collapses the can on to the fuel element. The elements are tested, first in a mass spectrometer for helium leakage and secondly by radiography to ensure that the welds are perfect. The cooling fins which are sometimes distorted during pressurization are straightened and the whole assembly cleaned using ultrasonic waves in citric acid. Formerly the cans were pressurized by heating in carbon dioxide for four hours at 500°C at a pressure of 350 lb/in²; a temperature of 500°C for four hours seems dangerously high for magnesium.

Although the handling of uranium involves certain special precautions—due to the emission of alpha particles and like lead, uranium dust can be a cumulative poison—the whole process appears to conform to fairly standard metallurgical practice.

Some development work is also being carried out at Springfield on the production of uranium hexafluoride for the enrichment plant at Capenhurst and on the development of new types of fuel elements. One design is being investigated for BICEPS —British Industrial Collaborative Experimental Programme, which carries out joint research for the five groups of firms building nuclear power stations in the United Kingdom, the Central Electricity Generating Board and the U.K.A.E.A.—which uses a uranium metal tube instead of a rod and would have the advantage that a graphite rod could be included in the central hole; the larger surface area would give better heat transfer characteristics.

Although the conversion of uranium concentrates to natural uranium fuel elements will soon be an established and standard process there is still a good

deal of reluctance to give simple information; this was attributed to commercial competition from the United States. Government financed bodies are rarely equipped, nor indeed should they be so equipped, to deal with commercial competition and it was therefore good to learn that, according to Sir William Cook, the authority would be prepared to consider transferring the manufacture of natural uranium fuel elements to industry at some future date.

Float Glass

The recent announcement in London by Sir Harry Pilkington of the development in St. Helens, Lancashire, of the float glass process provided an opportunity for comparing the optical properties of sheet glass and plate glass with those of samples of the new material. Surface wrinkles in sheet glass frequently amount to ten thousandths of an inch while twin ground plate glass —the best quality previously available—rarely varies by more than about one third of this amount. Typical surface flatness curves exhibited by the makers indicate that float glass is exceptionally parallel and free from distortion, surface irregularities being less than one thousandth of an inch on average.

In the float process, molten glass up to 100 in. wide is led, in one continuous ribbon about $\frac{1}{4}$ in. thick, from the glass furnace on to the surface of a bath of liquid metal, the temperature of which is carefully regulated. Gas heaters above the liquid metal bath provide a fire polishing zone from which the glass passes to a cooling zone—a controlled atmosphere is used to prevent oxidation of the metal in the bath—where its temperature is reduced sufficiently to allow both surfaces of the glass ribbon to harden enough to withstand mechanical handling. Thereafter it passes through an annealing lehr and on to cutting and grading machines for storage or dispatch. The process is continuous, and is at present operated on a three-shift basis.

Pilkington's claim that float glass is produced with fire polished surfaces brighter than those achieved by grinding and polishing. The output of the process is not limited or controlled by any property of the glass such as viscosity and it is possible, therefore, to process as much glass as the furnace can melt. It is understood that it has taken seven years to develop the process and that no changes in raw materials or glass composition are involved. The glass has been tested for windscreen making by the Triplex Safety Glass Company for an appreciable period of time.

Standard of Weight and Length

The Directors of the standards laboratories in the United Kingdom, the United States, Canada, New Zealand, South Africa and Australia have agreed to adopt an international yard which will be defined as equal to 0·9144 metre and an international pound equal to 0·453,592,37 kg all non-metric calibrations carried out by any of these laboratories after July 1959 will be based on the agreed international units.

The values of the yard in current use in the British Commonwealth and the U.S. in terms of the metre are as follows:

1 imperial standard yard	=0·914,397,2 m
1 Canadian yard	=0·914,4 m
1 yard as used by N.P.L.*	=0·914,398,41 m
1 United States yard	=0·914,401,83 m

The imperial standard yard is about 0·0002 inches shorter than the United States yard—the latter is defined in terms of the metre—and it continues to decrease in length at a rate of about one millionth of an inch each year. The consequent errors in the measurement of length are therefore of considerable importance in modern precision engineering. For example, it may be necessary to know the length of gauges accurately to one part per million while the permissible error on accurate yard scales is 0·0001 in.

The values for the pound in current use are:

1 imperial standard pound	= 0·453,592,338 kg
1 Canadian pound	= 0·453,592,43 kg
1 U.S. pound	= 0·453,592,4277 kg

The imperial standard pound is thought to have diminished in weight by about seven parts in ten million since 1846 and it is about two parts in ten million smaller than the United States and Canadian pounds which have been defined in terms of the international prototype kilogram. Although in this case the discrepancy is unimportant for practical engineering purposes it is highly unsatisfactory to have such independently defined standards.

It is curious to find, however, that although these international units conform to the recommendations of the Board of Trade Committee on Weights and Measures Legislation, the units will have no statutory value in the United Kingdom and ' may not be used for trade purposes in this country '. The units which must be used for trading are still the imperial units laid down in the Weights and Measures Act of 1878.

* This value is based on the length of the imperial standard yard in 1922.

BOOK REVIEWS

The Kinetics of Vinyl Polymerization by Radical Mechanisms

C. H. Bamford, W. G. Barb, A. D. Jenkins and P. F. Onyon

(*xii+318 pp; 8½ in. by 5½ in.*)
London: Butterworths Scientific Publications.
New York: Academic Press. 50*s*, $8.80

This book is a welcome addition to the considerable number of publications now available in the field of polymer chemistry. It will be of particular interest to chemists who, for the first time, wish to acquire an up-to-date knowledge of the mechanism and kinetics of free radical polymerization, and for those who are already actively engaged in research on polymerization kinetics it will provide a valuable critical review of the subject. By confining their attention to free radical mechanisms and only briefly discussing emulsion polymerization, the authors have succeeded in covering the field adequately in about 300 pages. They have intentionally and wisely omitted to discuss Ziegler type polymerization as the present is not the right time for a detailed review of this subject.

The first two and the final chapter are mainly theoretical, the former dealing with the derivation of the kinetic equations and the evaluation of the individual velocity coefficients for the propagation and termination reactions, while the latter deals with statistical aspects of polymerization and includes molecular weight distribution, size and composition distributions in copolymers, crosslinking and gelation. The central four chapters comprise a critical review of experimental results on homogeneous and heterogeneous polymerization, copolymerization, the initiation, retardation and inhibition processes. They also include some theory related to these topics, *e.g.*, the copolymer composition equation and kinetic equations for chain transfer and retardation are derived.

Of homogeneous polymerizations, styrene, methyl methacrylate and vinyl acetate have been the most widely studied and consequently most of chapter 3 is devoted to these polymerizations. About a third of chapter 4 is taken up in discussing the bulk polymerization of acrylonitrile, while the remainder includes the polymerizations of vinyl chloride and vinylidene chloride, the copolymerization of maleic anhydride and styrene, polymerizations in the presence of precipitants, vapour phase, popcorn, suspension and emulsion polymerizations. The chapter on copolymerization discusses copolymer composition, the significance of monomer reactivity ratios and φ factors, chain transfer, semi-vinyl polymerization including polysulphones and the theory of ceiling temperature, graft and block copolymers. Efficiency of initiation is dealt with in chapter 6, and initiation by peroxides, aliphatic azo-compounds and N-nitrosoacylarylamines are discussed in detail.

Numerous references, some as recent as 1957, to original papers are included at the end of each chapter, but a few omissions were noted. The subject index is quite good, but there is no author index. The book is well produced and remarkably free from printer's errors.

The reader who is familiar with the research publications of the four authors will no doubt detect a bias towards their particular interests in certain chapters. This is to be expected and does not detract from the value of the book; it offers an excellent account of the mechanism and kinetics of radical polymerizations and can be recommended without reservation to all chemists interested in this subject.

W. I. Bengough

Phosphorus and its Compounds—Vol. I, Chemistry

J. R. van Wazer

(*viii+954 pp; 9¼ in. by 5¾ in.*)
New York and London: Interscience. 208*s*

The organic chemistry of carbon has stood apart for so long from the rest of chemistry that it is exciting to review a book which may well guide and stimulate the development of the chemistry of a further element to a comparable level. Dr van Wazer as assistant research director and senior scientist of the Inorganic Chemical Division of the Monsanto Chemical Company, has made substantial contributions by his published work to our knowledge and understanding of the chemistry of phosphorus, in particular the condensed phosphates. In presenting this account of phosphorus chemistry in the light of current chemical theory, he has accomplished a feat of great value, drawing together current ideas and theories into a coherent whole, examining critically the mass of factual information, much of it a legacy from the dark days of the infancy of phosphorus chemistry, and suggesting innumerable further lines of development.

In the first volume of this two volume work, the early chapters concentrate on the essential fundamentals of atomic and valency theory as it affects phosphorus, and in so doing set the tone of much of the later sections of the book. In particular, the impact of nuclear magnetic resonance on phosphorus chemistry is clearly and forcibly put, an aspect with which the author has been very closely connected. The chemistry is covered under general compound types such as halides, hydrides, oxides, sulphides, *etc*, no limit being set on the subject matter, organo-phosphorus compounds being discussed along with the purely inorganic compounds. The theme of the book is 'phosphorus chemistry', a discipline in its own right rather than either 'inorganic-' or 'organic-phosphorus chemistry'.

The five chapters devoted to the phosphates deal with this complex field with particular clarity and underline the personal experience of the author in the chemistry of these compounds. The fascinating group of the compounds in which nitrogen is bound to phosphorus is discussed, the phospho-nitrilic chlorides being singled out for special mention in view of their current importance both in theory and practice.

No author writing on phosphorus chemistry can escape the dilemma of nomenclature. It is to be hoped that

Dr van Wazer's very cogent comments on this subject will not pass unnoticed by those responsible for settling the problems of phosphorus nomenclature.

No one connected in any way with phosphorus chemistry can fail to find this book stimulating. Perhaps it may encourage further workers to enter this interesting and promising field and thereby hasten the time when phosphorus chemistry possesses an equal standing to organic chemistry — one hopes so. For the non-specialist, particularly the teacher, this book should be consulted to see how the chemistry of an element more complex in many ways than carbon can be developed from a few basic concepts. D.S.P.

Handbook of Automation, Computation and Control—Vol. I

E. M. GRABBE, S. RAMO and D. E. WOOLDRIDGE (*Eds*)

New York: Wiley; London: Chapman & Hall. $17.00, 136*s*

THIS is the first volume in a series of three and the subject matter rather belies the title since the first fifteen chapters are concerned not with automation and computing but with the basic mathematical techniques involved in these subjects. However, as the editors' aim is to provide a self-contained reference book, it will perhaps be useful to see how these fit the general framework of the whole.

The book begins with three chapters on algebriac preliminaries, followed by chapters on difference, differential and integral equations, and complex variable theory. The next few chapters are concerned with operational calculus, conformal mapping and short accounts of Boolean algebra, probability and statistics. The material has been very much condensed with the result that it will be intelligible only to readers who have already acquired a knowledge of the subject from other authorities, and occasionally, as in the discussion of Sturm's theorem on page 204, the text is misleading as well as being incomprehensible. The authors have, however, been able to reduce all of the most useful material into a reasonably short compass.

The second main section, chapter 14, is concerned with numerical analysis and gives a clear, comprehensive account of the subject. It is followed by a section on operations research over 120 pages long, which is well written and more coherent than the other sections, possibly because it is the product of a single author. The collection of basic material ends with three chapters on information theory, on smoothing and filtering, and on data transmission.

The remainder of the book is concerned with the theory of feedback and its application to control. There are chapters on methodology, systems analysis, and stability—which follow well trodden paths—and a discussion of the relative merits of transient response and frequency response methods in design. A practical note is introduced by the two chapters on compensation and on the effects of noise and this is continued in the penultimate chapter which describes the methods of handling non-linear systems. The book ends on an up-to-date note with an account of sampled-data control systems.

The series will undoubtedly become a standard authority in its field and, although the preliminary mathematical survey will not be of much value to readers whose education has been in the British tradition, the remainder of the book can be strongly recommended. A. D. BOOTH

The Electrical and Mechanical Properties of Solids

N. CUSACK

(*xv+428 pp; 9 in. by 6 in.*)

London: Longmans, Green and Co. Ltd. 45*s*

THE author describes this book as an attempt to help reflect the great activity and achievement of modern solid state physics in a form accessible to undergraduates. The book is indeed a most successful attempt and is likely to be welcomed by both lecturers and students alike. There is little doubt that the several excellent texts on solid state physics which have appeared in recent years make hard reading for students in the early part of honours physics courses.

After a superficial introduction sketching some relevant properties of solids, the free electron gas model is dealt with, followed by a discussion of work function and contact potentials. The difficulties which beset these topics are well brought out.

Thermionic and photoelectric emission are followed by an account of thermoelectricity in which both thermodynamic and electron gas aspects are well treated. The uses and limitations of classical treatments of electrical conduction are followed by an excellent elementary approach to band theory. Considerable space is devoted to discussion of semiconductors, mainly germanium and silicon. (Although the author intentionally excludes technical devices, it may be felt that the transistor is so important as to deserve mention.)

The treatment of magnetism includes recent work on relaxation and resonance. Ferromagnetism is treated mainly phenomenologically with rather little comment on exchange interaction. The difficulties in the way of a satisfactory description of superconductivity are well brought out in a section which summarizes some of the most recent work in this field. The book concludes with chapters on dielectrics and on dielectric oddities such as pyroelectricity, piezoelectricity and ferroelectricity.

Throughout the book ample references are given to recent work in the fields discussed, an invaluable feature for the post-graduate student at the start of his work. By restricting mathematical arguments to an elementary level, Dr Cusack succeeds in keeping to the fore the physical principles under discussion. The result is admirable and the book may be thoroughly recommended. O. S. HEAVENS

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